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Dissertation

THE EFFECT OF AMMONIUM CHLORIDE WASH SOLUTION ON THE QUANTITATIVE GRAVIMETRIC DETERMINATION OF IRON
and
THE LEAD-URANIUM-THORIUM RATIO OF URANINITE FROM SPRUCE PINE, NORTH CAROLINA

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ONE

THE EFFECT OF AMMONIUM CHLORIDE WASH SOLUTION ON THE QUANTITATIVE GRAVIMETRIC DETERMINATION OF IRON

I. INTRODUCTION

In the gravimetric determination of iron the usual method involves the oxidation of the iron to the ferric state, precipitation as hydrated ferric oxide, commonly called ferric hydroxide, and subsequent ignition to Fe_2O_3. The matter of washing the precipitate is of considerable importance, especially in view of the fact that we are dealing with a gelatinous material. Water might be a satisfactory washing agent if solubility were the only determining factor in making a choice. Since hydrated ferric oxide is so extremely insoluble, no appreciable loss should be experienced through dissolution. Water, however, is not an altogether suitable washing agent due to the fact that the precipitate is colloidal and may be peptized if washed with pure water containing no electrolytes. In order to prevent peptization it is advisable to wash with a solution of some electrolyte which, of course, must be easily volatile on the subsequent ignition of the precipitate. The three electrolytes which have been recommended and which are frequently used are ammonia, ammonium chloride, and ammonium nitrate. The literature on the relative value of these three agents is rather confusing.

Apparently the only critical study which has been made is that of Daudt[1], who carried out a few experiments

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[1] Daudt, Ind. and Eng. Chem., 7, 847 (1915)

on the use of ammonium chloride. He analyzed a solution of ferric chloride of known concentration, varrying the amounts of ammonium chloride in the wash solution. His results are shown in the following table:

% of NH_4Cl in the wash solution	0	0	1	1	5	10	10
% Fe found	99.80	99.87	99.87	99.87	99.55	97.20	94.04

He called attention to the appearance, during the ignition of a precipitate washed with ammonium chloride solution, of a film of brown sublimate on the inner edge of the crucible and on the bottom of the crucible lid. The results, although only a few analyses were carried out, indicate that there was no loss of iron due to volatilization of ferric chloride if the precipitate was washed with a solution of ammonium chloride as dilute as one per cent. The loss when a five per cent solution of ammonium chloride was used was quite appreciable.

A brief comment on this problem, however, appears in an article by Kunz and Bailey[1] on an investigation of the gravimetric determination of iron as ordinarily carried out as a laboratory experiment in elementary courses. The major part of their research was evidently designed to

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[1] Kunz, A.H., and Bailey, G. Sterling: The Gravimetric Determination of Iron; J. Chem. Ed. 11, 247 (1934)

show that "the use of ammonia solution which has been in contact with glass is very detrimental to the gravimetric iron determination". But in order "to prove even more definitely that there is no possibility of loss of iron by volatilization when ferric hydroxide is ignited in the presence of ammonium chloride, equal volumes of ferric chloride solution were precipitated with ammonia in the usual manner. Three of the samples were filtered, dried, and ignited without washing. Two samples were washed free of chlorides before ignition." The results were as shown:

Method	Number of determinations	Mean grams of iron
Washed	2	0.2903
Unwashed	3	0.2901

Since the "usual manner" referred to above involved dilution of the solution to 200 ml, the ordinary process of filtration would pass most of the chloride into the filtrate. Even so it is interesting to note that in spite of the low concentration of chloride remaining, a loss of .2 mg of iron occurred in the cases involving ignition in the presence of chlorides. The authors felt that this was not significant; but attention should be called to the fact that the results of their five analyses are in harmony with the conclusions of this dissertation.

The textbooks commonly used in courses in quantitative analysis vary widely in their directions for the washing of the precipitate in the determination of iron.

Willard and Furman state[1] "Ammonium nitrate is most satisfactory (as a wash solution), since it aids somewhat in the subsequent ignition of the precipitate. Ammonium chloride is unsuitable, because during the ignition ferric chloride may be formed which is volatile even below red heat.

$$Fe_2O_3 + 6\ NH_4Cl \longrightarrow 2\ FeCl_3 + 6\ NH_3 + 3\ H_2O$$

"A similar action does not occur with aluminum oxide. Because of this action between ferric oxide and a chloride, it is desirable to wash out nearly all the ammonium chloride present in the ferric hydroxide, although very small amounts will not react with the oxide."

Kolthoff and Sandell state[2] that "it is perfectly safe to ignite a precipitate of iron which has been washed with a 1 per cent solution of ammonium chloride without first washing out most of the chloride".

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[1] Willard and Furman: Elementary Quantitative Analysis, page 321. (D. Van Nostrand Company, 1935)

[2] Kolthoff and Sandell: Textbook of Quantitative Inorganic Analysis, page 298. (Macmillan Company, 1936)

Treadwell and Hall[1] direct the analyst to wash the precipitate "with hot water or hot 2 per cent ammonium nitrate solution until free from chloride. Do not wash with ammonium chloride solution because ferric chloride is volatile upon ignition."

In view of the conflicting opinions among analysts as to the best washing solution to use and because of the paucity of research which has been done on this important problem, this systematic study was undertaken.

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[1] Treadwell and Hall: Analytical Chemistry, Volume II, Quantitative Analysis, Eighth Edition, page 99. (John Wiley and Sons, 1935)

II. EXPERIMENTAL PROCEDURE

About fifty grams of reagent grade ferric nitrate were dissolved in a liter of distilled water. Ten milliliters of concentrated nitric acid were added to prevent hydrolysis. This solution was shown to be free from ferrous ions by testing with potassium ferricyanide. Reagent grade ammonium chloride was dissolved in distilled water to make a ten per cent solution which was later diluted as required. Reagent grade ammonium nitrate was dissolved and diluted to make a one per cent solution. These ammonium salt solutions were shown to be iron free by testing with ferrocyanide and thiocyanate. Ammonia was distilled immediately before use.

Ten gram samples of a solution of ferric nitrate were weighed by difference from a weight buret suspended from the left hand pan of the balance. A counterpoise of the same general shape was suspended from the right hand beam. When not in the balance case, the weight buret and the counterpoise were suspended from hooks at each end of a short bar held in a horizontal position by a clamp on a ring stand. The ring stand and bar were wound with cloth to prevent any flakes of iron rust from falling into the beakers. All ring stands used were painted at frequent intervals. Suitable loops in the platinum wire wound around the buret and the counterpoise made it possible to hang them on the hooks of the bar as well as on the

hooks on the beam of the balance.

Whenever it was desired to remove a sample, the buret was hung from the support, a clean beaker was placed below it, and the proper amount of solution was allowed to flow into the beaker. A clean piece of cloth was used to cover the fingers while grasping the buret and turning the cocks so that they would not touch the glass. A weight accurate to five significant figures was obtained by weighing the ten gram sample to the nearest milligram.

The first method of precipitation was as follows: The samples were treated with 2 ml of nitric acid, boiled five minutes, precipitated with an excess (determined by the odor) of freshly distilled ammonia, boiled five minutes longer, and the precipitates allowed to digest over night. The precipitates were then filtered, washed several times with 1 % ammonium nitrate, and ignited to constant weight in the usual manner.

It was intended to analyse the solution several times until its concentration was accurately known. Then the variations from this known concentration which resulted from washing the precipitates with ammonium chloride could be determined. It was noted, however, that the concentration of the solution increased slightly between the first and second analyses. The per cent of iron increased from

0.574 % to 0.579 % in about three weeks. In an attempt to prevent this loss, which was believed to be due to evaporation of water, the ground glass joints of the buret were covered with a thin film of stopcock grease. The results of subsequent analyses varied widely and it was noticed that the weight buret lost weight rapidly on the balance. It was concluded that these errors were due to evaporation of a volatile solvent from the grease, and the joints were therefore thoroughly cleaned to remove all the grease. This treatment decreased, but did not prevent, the loss noted.

Because of the changes in the strength of the solution due to evaporation, the per cents of iron as determined in a given set of analyses were not compared with the results of any other series. In each series of analyses, therefore, weighed samples were precipitated; half of them were washed with one per cent ammonium nitrate solution, while the other half were washed with ammonium chloride solution of the desired concentration. Approximately 10 ml samples were carefully weighed from the counterpoised weight buret. Both sets of samples were diluted to 190 ml, heated on the steam bath for thirty or forty minutes, and treated with 15 ml of freshly distilled ammonia. The precipitates were digested for one hour on the steam bath, allowed to stand over night, and filtered. The precipitates thus obtained

were crystalline and ideal for filtering except for one very unfortunate fact: namely, the presence in the solution of colloidal ferric oxide which was formed by the hydrolysis of the ferric nitrate during the preliminary heating. During the precipitation and the digestion which followed, this colloidal ferric oxide was often coagulated; but too frequently it was not. The precipitates almost invariably went through the pores of #40 Whatman filter paper. The #42 paper was better and usually satisfactory; but many analyses were ruined because part of the precipitate was lost in this way.

This hydrolysis did not occur in the first analyses performed because 2 ml of nitric acid were added to each sample and the resulting concentration of electrolyte was sufficient to prevent it. It was finally discovered that if the preliminary heating was omitted and the diluted solution was treated while cold with 10 ml of ammonia and then digested on the steam bath for one hour, a firm precipitate which was readily retained by #40 paper was obtained.

The supernatant liquor was poured through the filter and the precipitates transferred to the filter paper as rapidly and as completely as possible by a stream of solution from a wash bottle. The last traces were removed from the beaker by wiping the sides with pieces of filter

paper. The necessary allowance was made for the weight of the ash of all the paper used. The precipitate on the filter was thoroughly washed with at least ten portions of the selected washing solution in order to wet thoroughly each precipitate with that solution.

The well-drained but still wet precipitate and paper were then placed in a previously ignited and weighed Vitrosil crucible. The ignition was begun by placing the crucible in a four inch porcelain evaporating dish which served as a radiator. The evaporating dish was then supported on a tripod by means of a wire triangle and heated with the smallest flame of a Tirrell burner until the paper and precipitate were completely dry.

From this point on two different procedures were followed. The first, hereinafter referred to as slow ignition, was to increase gradually the flame beneath the radiator until the paper was completely charred, but without allowing any pronounced smoke or fumes to be produced. This process required about three hours and should have given the maximum opportunity for any possible reaction between the precipitate and the reagent contained in the wash solution with which the precipitate was wet. The second procedure, hereinafter referred to as rapid ignition, was to increase the flame just as rapidly as possible without causing the paper to burst into flame. This

process required from twenty to thirty minutes to complete the charring of the paper. In both procedures, after the paper had been completely charred, the precipitates were ignited to constant weight over Meker burners. It should also be understood that the entire process was continuous with no break between the preliminary drying, the charring of the paper, and the final high temperature ignition.

In order to determine whether or not the variations may have been caused by silica removed from the pyrex beakers by the ammoniacal solutions during digestion, a series of blanks was run. A volume of 200 ml of water was treated with 10 ml of freshly distilled ammonia, digested for one hour on the steam bath, and allowed to stand forty-eight hours (more than twice the usual time) before filtering. The usual amount of wash solution (about 150 ml) was poured through the filter. The average increase in weight of the ten crucibles for the ten blanks, after deducting the weight of the ash of the filter paper, was 0.10 mg, the median was 0.13 mg, and the maximum gain was 0.25 mg. Only two samples exceeded 0.16 mg. Since the actual losses in almost every case exceed even the maximum figure, it may be concluded that the variations are not due to silica.

The weights used were standardized by the Richards method and all weights given are corrected to vacuum. In the tables of results, analyses having the same letter

prefixed to the sample number are comparable, as all samples with the same letter were weighed out at the same time.

III. DISCUSSION OF RESULTS

The question which this research was designed to answer is: "Will there be any significant error in the results of a gravimetric analysis of iron as ordinarily conducted in the laboratory if the precipitates are washed with ammonium chloride instead of ammonium nitrate?"

It is a well known fact that ammonium chloride, when heated, dissociates into ammonia and hydrogen chloride. The hydrogen chloride might react with the hydrated ferric oxide to form ferric chloride. Since the ferric chloride is volatile at the temperature used in the ignition of the precipitates, the results obtained when an ammonium chloride washing solution is used should be low if there is appreciable reaction between the oxide and the hydrogen chloride.

The data in Table I show that in every case where the precipitates were dried slowly, the average of those analyses in which ammonium chloride was used was lower than that in which ammonium nitrate was used in the washing solution. In individual analyses, this loss was not always noted, and the magnitude of the loss was quite variable in many series of analyses. One would not expect the loss to be constant, however, for if the essential reaction is between the ferric oxide and hydrogen chloride, the amount of loss will depend upon the opportunities which these

substances have to react. If the precipitate is smothered at the bottom of the crucible by layers of damp filter paper, the hydrogen chloride will be retained in contact with the ferric oxide for a longer time than if the arrangement of the precipitate and paper allows more adequate ventilation. Other variable factors, such as the relative wetness or dryness of the precipitate and paper at the beginning of the ignition, or the rate of heating during the ignition, may have an indeterminate effect on the amount of ferric chloride formed.

To the analytical evidence that the use of ammonium chloride does cause low results in the analysis of iron may be added the following direct evidence. One milliliter of 10 % ammonium chloride solution was added to each of four crucibles containing weighed precipitates of Fe_2O_3, and one milliliter of 5 % ammonium nitrate solution was added to each of two crucibles containing similar precipitates. The crucibles were carefully dried and then ignited. The crucibles and precipitates which had been treated with ammonium nitrate decreased in weight 0.00006 and 0.00001 grams. This loss is negligible, being within the error of weighing. The crucibles and precipitates which had been treated with ammonium chloride decreased in weight 0.00015, 0.00025, 0.00310, and 0.00293 grams. From the last two crucibles a yellowish brown vapor was

observed during ignition. Some of this sublimate condensed at the top of the crucible and gave a red deposit of ferric oxide. This loss of weight is not only significant in itself, but is supported by the visual evidence of the sublimate. The wide differences emphasize the lack of reproducibility due to slight differences in the rate of heating.

One of the most interesting products of this investigation is the evidence concerning the effect of the rapidity of drying and igniting the precipitated and washed ferric hydroxide. It seems reasonable to suppose that if the ammonium chloride and its dissociation products were volatilized quickly, the time of contact between any hydrogen chloride produced and the precipitate would be so short that practically no ferric chloride would form.

All of the textbooks insist that the ignition should be carried out slowly and carefully. "The heating should be slow".[1] "Always in igniting precipitates care should be taken to raise the temperature slowly".[2] Two obvious errors may result from two rapid ignition: first, small particles of the precipitate may be carried out of the

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[1] Kolthoff and Sandell, op. cit. p247

[2] Treadwell-Hall, op. cit. p 38,39

crucible by the rising smoke; second, the precipitate may be reduced by the hot carbon. Treadwell and Hall[1] point out another source of error: namely, that rapid ignition "may fuse a little salt around the ash of the paper and carbon inside such a fused coating is hard to burn because it is out of contact with the air". This difficulty is especially likely when silica is present. It has been shown that, on the average, a tenth of a milligram of silica may be present. We might expect, therefore, that if the heating is forced, the loss due to volatilization of ferric chloride would be reduced to a minimum; but that other inaccuracies, positive and negative, due to the factors just cited might cause the results to vary widely. The erratic results reported in Table II illustrate this point.

Table II shows that the losses with ammonium chloride average much less in the case of rapid charring than in the case of slow charring. The results usually indicate a loss, however, and do not check well among themselves. Too great haste in igniting the precipitates should, therefore, be avoided.

A few experiments were performed in which a comparison could be made of the relative value of hot water,

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[1] Treadwell-Hall, op. cit. p 40

ammonium hydroxide, and five per cent ammonium nitrate. Table III shows the results of these experiments.

Freshly distilled 1.37 % ammonia gave satisfactory results. Due to the possible solvent action of this solution on glass, however, this washing agent is not to be preferred to ammonium nitrate. Hot water gave low results, probably due to peptization of the colloidal precipitate, permitting it to be lost through the filter paper. The results with five per cent ammonium nitrate were not as good as with one per cent ammonium nitrate, but were not significantly different.

It was a noticeable fact in this research that whenever ammonium nitrate was used as a wash solution, the charring of the filter paper was accomplished much more easily and left less apparent ash than when ammonium chloride was used. This observation corroborates the statement of Willard and Furman[1] that ammonium nitrate "aids somewhat in the subsequent ignition of the precipitate".

The brown sublimate mentioned by Daudt was often seen on the upper folds of the filter paper during heating. It had the characteristic color of ferric chloride.

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[1] Willard and Furman, op. cit., p 321

Deposits of red oxide were often found on the sides of the crucible. It was never noticed as a brown vapor except when the precipitates were ignited with ammonium chloride directly.

All the evidence obtained in this investigation points to the fact that ammonium chloride is undesirable as a component of the wash solution for hydrated ferric oxide. If the precipitates are ignited slowly, the results obtained when the wash water contains two or more per cent of ammonium chloride are definitely lower than the results obtained when the wash water contains ammonium nitrate. The results obtained when the wash water contains one per cent of ammonium chloride are only slightly lower; but they are consistently lower. It would be expected that if less loss occurs with 2 % ammonium chloride than with 4 %, that still less loss would be obtained with 1 % than with 2 %; but that the loss, even if small, would be definite. The experimental results indicate that this is a fact. If the precipitates are ignited rapidly, less loss occurs; but some loss occurs and the results do not check as well as with slow ignition. This effect of the speed of ignition may well account for the contradictory views held by many chemists as to the effect of ammonium chloride in the wash solution.

Therefore it may be stated that the presence of ammonium chloride in the wash solution has no advantages whatsoever, that the losses caused by its presence are analytically significant, and that if chloride ions are present in the solution analyzed, the possibility of the formation of ammonium chloride should be avoided by washing the precipitate with a solution of ammonium nitrate until all chloride ions are removed.

Tables

The following tables show the analytical results obtained in the individual analyses. The first column gives the number of each sample for purposes of identification. The results prefixed by the same letter were weighed out at the same time and are comparable. The second column shows the vacuum weight of each sample and the third column shows the net vacuum weight of the precipitate actually obtained in each case. The results for which a per cent of Fe_2O_3 are given (column four) were obtained from precipitates which were washed with ammonium nitrate (1 %) and are assumed to be correct for the purpose of calculating the losses suffered when the precipitates were washed with some other solution. The individual weights of the samples in these other cases were multiplied by the average value for the per cent of ferric oxide obtained for this series and the product recorded in the fifth column as the weight of the theoretical precipitate. This weight is considered to be the weight of precipitate which should have been obtained from each sample if there had been no loss caused by the washing solution. Thus the average of the per cents of ferric oxide obtained in samples C 4, C 5, and C 6, multiplied by the weight of the sample C 1 (9.722) gives 0.09021 as the weight which should have

been obtained. Since the actual weight was 0.09019, the loss in this case was 0.02 mg. The losses are recorded in the last column.

Table I

Results obtained by slow ignition when the precipitates obtained were washed with 1 % ammonium chloride

Sample number	Weight of sample	Weight of precipitate	Per cent of Fe_2O_3	Weight of theoretical precipitate	Loss in milligrams
C 4	11.4108	.10593	.92834		
C 5	11.8764	.11016	.92756		
C 6	16.3941	.15200	.92718		
C 1	9.722	.09019		.09019	.00
C 2	12.2074	.11315		.11325	.10
C 3	12.3681	.11458		.11474	.16
F 7	11.5522	.12239	1.0594		
F 8	11.0917	.11749	1.0592		
F 10	11.9632	.12667		.12673	.06
F 11	11.1908	.11804		.11855	.51
F 12	11.2979	.11879		.11968	.89
G 22	10.7514	.11242	1.0456		
G 23	11.2914	.11812	1.0461		
G 24	12.9497	.13541	1.0457		
G 19	10.1427	.10569		.10608	.39
G 20	11.5007	.11981		.12028	.47
G 21	11.2389	.11717		.11754	.37
H 34	11.3116	.11848	1.0474		
H 35	11.7204	.12269	1.0467		
H 31	9.2546	.09648		.09690	.42
H 32	11.7628	.12269		.12317	.48
H 33	11.3698	.11912		.11905	.07 (gain)

Results obtained by slow ignition when the precipitates obtained were washed with 2 % ammonium chloride

B 19	12.1409	.10189	.8392		
B 22	10.8811	.09123	.8384		
B 18	11.3606	.09497		.09530	.33
B 24	17.2530	.14418		.14472	.54
D 10	11.9845	.11223	.93646		
D 11	13.3152	.12458	.93564		
D 12	11.5048	.10771	.93622		
D 7	12.4252	.11583		.11631	.48
D 8	11.3049	.10542		.10583	.41
D 9	11.9008	.11099		.11140	.41

Results obtained by slow ignition when the precipitates were washed with 2 % ammonium chloride (continued)

Sample number	Weight of sample	Weight of precipitate	Per cent of Fe_2O_3	Weight of theoretical precipitate	Loss in milligrams
I 40	10.8048	.11467	1.0613		
I 41	11.4013	.12106	1.0618		
I 42	12.7775	.13573	1.0624		
I 37	10.0818	.10678		.10705	.27
I 38	11.3660	.12015		.12069	.54
I 39	11.0630	.11710		.11747	.37
J 47	12.3413	.12921	1.0470		
J 48	10.0406	.10499	1.0457		
J 44	11.4994	.11986		.12032	.46
J 45	11.4027	.11869		.11932	.63
K 52	11.0741	.11588	1.0464		
K 53	11.9484	.12502	1.0464		
K 50	11.1112	.11612		.11626	.14
K 51	11.9820	.12482		.12538	.56

Results obtained by slow ignition when the precipitates were washed with 4 % ammonium chloride

B 19	12.1409	.10189	.8392		
B 22	10.8811	.09123	.8384		
B 17	13.2799	.11027		.11140	.13
B 20	10.7772	.08982		.09040	.58
B 23	13.4107	.11172		.11250	.78
L 58	10.8193	.12265	1.1336		
L 59	12.2555	.13887	1.1332		
L 55	11.5704	.13057		.13114	.57
L 56	11.7720	.13292		.13342	.50

Results obtained by slow ignition when the precipitates were washed with 5 % ammonium chloride

E 1	13.7340	.14011	1.0202		
E 5	9.2823	.09488	1.0222		
E 4	11.3295	.11435		.11490	.55
E 6	13.2565	.13379		.13537	1.58
Q 114	12.9254	.14670	1.1350		
Q 115	9.7515	.11063	1.1345		
Q 109	9.3149	.10529		.10570	.41
Q 110	10.8325	.12240		.12292	.52
Q 111	11.4030	.12919		.12940	.21

Table II

Results obtained by rapid ignition when the precipitates were washed with 2 % ammonium chloride

Sample number	Weight of sample	Weight of precipitate	Per cent of Fe_2O_3	Weight of theoretical precipitate	Loss in milligrams
T 130	14.4769	.21546	1.4883		
T 131	12.8262	.19136	1.4920		
T 127	12.5775	.18713		.18742	.29
T 128	12.4961	.18600		.18620	.20
T 129	12.9962	.19292		.19366	.74
U 134	12.7068	.18851	1.4835		
U 135	14.3715	.21304	1.4824		
U 132	12.7364	.18879		.18887	.08
U 133	14.2721	.21132		.21164	.32
U 136	10.1880	.15103		.15109	.06
V 138	12.1409	.18090	1.4900		
V 139	13.6669	.20315	1.4864		
V 137	12.4479	.18540		.18525	.15 (gain)
V 140	13.7201	.20384		.20416	.32

Results obtained by rapid ignition when the precipitates were washed with 5 % ammonium chloride

Sample number	Weight of sample	Weight of precipitate	Per cent of Fe_2O_3	Weight of theoretical precipitate	Loss in milligrams
O 100	11.0806	.12567	1.1344		
O 161	10.6662	.12101	1.1345		
O 102	12.5024	.14179	1.1341		
O 97	10.6333	.12042		.12061	.19
O 98	10.3387	.11727		.11726	.01 (gain)
O 99	10.8252	.12297		.12279	.18 (gain)
Q 114	12.9254	.14670	1.1350		
Q 115	9.7515	.11063	1.1345		
Q 112	10.6853	.12114		.12124	.10
Q 113	11.9875	.13564		.13603	.39

Table III

Results obtained when the precipitates were washed with ammonia, hot water, and 5 % ammonium nitrate

Sample number	Weight of sample	Weight of precipitate	Per cent of Fe_2O_3	Weight of theoretical precipitate	Loss in milligrams
		Washed with 1.37 % ammonia			
P 106	10.7616	.12299	1.1431		
P 107	12.6343	.14457	1.1443		
P 108	11.6102	.13284	1.1442		
P 103	10.7580	.12296		.12305	.09
P 104	11.3404	.12979		.12972	.07 (gain)
P 105	11.1621	.12772		.12768	.04 (gain)
		Washed with hot water			
R 120	13.4153	.15306	1.1409		
R 121	12.6513	.14437	1.1409		
R 116	12.2316	.12782		.12814	.32
R 117	11.5339	.13143		.13159	.16
		Washed with 5 % ammonium nitrate			
N 94	12.3445	.13184	1.1315		
N 95	11.6514	.13966	1.1314		
N 91	11.6415	.13157		.13172	.15
N 92	10.7624	.12173		.12174	.01
N 93	11.2380	.12721		.12715	.06 (gain)

IV. CONCLUSIONS

The conclusions reached may be summed up as follows:

1. In the gravimetric determination of iron, hot water is not recommended as a washing agent due to possible peptization and subsequent loss of the precipitate.

2. Ammonia is not recommended as a washing agent due to its possible action on glass.

3. Dilute ammonium chloride solution is not recommended as a washing agent due to the possible formation and subsequent volatilization of ferric chloride. The magnitude of the resulting loss depends upon the concentration of the ammonium chloride solution and the method of drying and igniting the precipitate.

4. One or two per cent ammonium nitrate solution is recommended as the most satisfactory washing agent in the gravimetric determination of iron.

TWO

THE LEAD-URANIUM-THORIUM RATIO OF URANINITE
FROM
SPRUCE PINE, NORTH CAROLINA

I. INTRODUCTION

A. Methods used to calculate the age of the earth

Man has always been fascinated by the problem of the age and origin of his world. At the turn of the century the age problem had been approximately settled: by the estimate of G. H. Darwin of 57 million years, based on the separation of the moon from the earth; by the estimate of Lord Kelvin of 20 - 40 million years, based on the rate of cooling of the earth; and by the estimate of Joly of 80 - 90 million years, based on the accumulation of salt in the ocean[1]. The discovery of radioactivity upset all of these calculations.

The oldest method for calculating the age of the earth is based on the fact that if the depth of a sedimentary deposit and the rate of sedimentation are known, the age of this deposit can be calculated. According to Schuchert[2] the maximum thickness of strata on the North American continent deposited since the beginning of the Cambrian period is 259,000 feet. It has been estimated

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[1] Knopf, Adolph (editor): National Research Bulletin 80, The Age of the Earth, page 3

[2] ibid, page 3

that, when the other continents have been more thoroughly investigated and all the data combined, the total thickness for the world will total some 400,000 feet[1]. It is almost impossible to make even an approximate estimate of the age of these deposits, except in the case of certain individual deposits. For example, Bradley has suggested that the Green River formation is from five to eight million years old[2].

If the total salt content of the ocean and the rate at which the rivers of the earth are carrying salt into it are known, the age of the ocean can be calculated. The age, one hundred million years, obtained by Joly and by Clarke depends on two assumptions: first, that the rate at which sodium has been supplied to the ocean has been constant throughout geologic time; and second, that no sodium has been lost by the ocean. Both of these assumptions are known to be untrue. It is known that the rate of solvent denudation has varied widely and that sodium is removed from the ocean not only in wind born spray, but also by adsorption and base exchange with newly deposited sediments[3].

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[1] Knopf, Adolph, op. cit. page 4

[2] ibid, page 4

[3] ibid, page5

If the present size of the universe and the rate at which it is expanding are known, the age of the universe can be calculated. Eddington suggests that this theory of an expanding universe places the origin of the present order of things about 10,000 million years ago.[1]

If proper allowances are made for the heat produced by radioactivity, the age of the earth might be calculated from its rate of cooling. The conclusions reached by this method, however, do not seem to correspond with the conclusions of geological evidence[2].

There are three methods based definitely on radioactivity: the nature of pleochroic halos, the volume of helium, and the uranium - lead ratio.

In certain kinds of mica are spherical regions of discoloration, called pleochroic halos, which are caused by the alpha particles emitted by a small piece of radioactive material at the center. For each element in the uranium - radium series there is a definite range based on the fact that the ionizing power of an alpha particle is greatest just before it reaches the end of its path. From the amount of radioactive material at the center and from

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[1] Eddington, Sir Arthur: New Pathways in Science, page 67 (The Macmillan Company, 1935)

[2] Knopf, Adolph, op. cit., pages 3, 446

the number of alpha particles required to produce a discoloration of a given intensity (experimentally determined), the age of the mineral can be calculated. Since light and heat may affect the coloration, however, the method is not very accurate[1]. The chief importance of the data from the halos is that it demonstrates that the rate of disintegration of thorium and uranium has been constant over long periods of time[2].

The age of a mineral has also been calculated from the volume of helium contained in it[3]. For this purpose it must be assumed that all of the helium evolved by the disintegration of the radioactive elements has been retained by the mineral. But since the helium would probably escape to some extent when the mineral is ground in preparation for analysis, the method gives a minimum estimate only[4].

The most promising method for determining the age of a mineral is based on the determination of the lead which is present as a result of a radioactive disintegration.

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[1] Knopf, Adolph, op. cit. page 108

[2] ibid, page 145

[3] ibid, page 197

[4] ibid, page 106

This method is due to Boltwood, who arranged a number of minerals in the order of their lead - uranium ratio and showed that a higher ratio indicated an older mineral[1]. He assumed that all of the lead was the end product of the disintegration of uranium.

Uranium 238.0 expels eight alpha particles to form lead 206; thorium 232 expels six alpha particles to form lead 208. If 1/C represents the amount of uranium lead produced by one gram of uranium in a million years[2], the age of the mineral is given by the formula:

$$\text{Age} = \frac{\text{Pb}}{\text{U}} \cdot \text{C million years,}$$

where Pb and U are the percentages of lead and uranium in the mineral. If k represents the amount of uranium equivalent in lead production to one gram of thorium, the age of a pure thorium mineral would be given by the formula:

$$\text{Age} = \frac{\text{Pb}}{\text{k Th}} \cdot \text{C million years.}$$

If both uranium and thorium are present, the formula becomes:

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[1] Knopf, Adolph, op. cit., page 73

[2] ibid, pages 199 - 205

$$\text{Age} = \frac{\text{Pb}}{\text{U} + k\,\text{Th}} \cdot C \text{ million years.}$$

The values of C and k in the formulas given depend on the disintegration constants of uranium and thorium and on the atomic weights of the parent elements and of the final products. If we take Kovarik's value of 1.52×10^{-10} yr^{-1} for the disintegration constant of uranium, we obtain C = 7600. In a similar manner k is determined to be 0.36. The formula for the age of the earth then becomes:

$$\text{Age} = \frac{\text{Pb}}{\text{U} + 0.36\ \text{Th}} \cdot 7600 \text{ million years}^{1}.$$

The expression Pb/ (U + 0.36 Th) will be referred to as the lead ratio and the product of this ratio and 7600 as the approximate age.

In order to apply any method for measuring geological time, full consideration must be given to three kinds of data: first, the rate at which a given process is going on at the present day; second, the total change produced by the process throughout the time to be measured; and third, the law of variation followed by the process

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[1] Knopf, Adolph, op. cit., page 205

throughout the entire interval of time. The third condition is often disregarded; but it is of major importance. The lead method is the only one of those discussed above which approximates the conditions designated.

The validity of the lead method depends on three essential conditions[1]: first, the analytical work must be accurate; second, the mineral analyzed must have been lead free when crystalization occurred or it must be possible to allow for the presence of lead in the original crystal; and third, the mineral must have remained unaltered throughout the entire period to be measured.

Workers in the past have usually ground up the entire mineral on the assumption that it was of constant composition throughout; but if the crystal has been leached and the leaching was not uniform, the ratios are worthless.

Alter and Kipp[2] took a good crystal of uraninite and dissolved one third of it in nitric acid. The crystal was then washed and a second layer removed by nitric acid. The two layers and the core were then analyzed separately. The lead ratios obtained for the core and for the middle layer checked very well (0.188 and 0.187); while the ratio for

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[1] Knopf, Adolph: op. cit. page 427

[2] Alter and Kipp, American Journal of Science, 32, 120-128 (1936)

the outside layer (0.235) showed that leaching had occurred.

In order to avoid the criticism of preferential leaching by the acid, Yuill[1] divided a similar crystal into three layers with a file. David[2], in this laboratory, worked on a sample of uraninite from Spruce Pine, North Carolina, which he divided into three layers with a file. David's results were as follows:

Section of crystal	Per cent of insoluble material	Per cent of lead	Per cent of uranium	Per cent of thorium
Outside	2.342	1.836	59.587	0.739
	1.892	1.842		0.749
	1.744		59.897	0.719
(ave)	1.993	1.839	59.742	0.736
Middle	1.783	2.640	62.533	
	1.499	2.500	63.168	1.353
	1.772	2.557	63.067	1.329
(ave)	1.685	2.566	62.923	1.341
Core	0.485	2.328	51.911	1.350
	0.361	2.304	50.937	1.240
	0.473		51.085	1.364
(ave)	0.440	2.316	51.311	1.318

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[1] Yuill, Laura A., A.M. Thesis, Boston University, 1936

[2] David, Nasim A., A.M. Thesis, Boston University, 1938

B. Statement of the scope of this dissertation

Obviously the formula given for calculating the age of the earth can not be used with confidence unless the amounts of lead, thorium, and uranium have been accurately determined. It is proposed, therefore, to evaluate some of the methods used in the analysis of uranium minerals and then to apply the most satisfactory methods in the analysis of the mineral analyzed by David and reported above. Although the lead ratio of this mineral and its age will be calculated, the problem is essentially a chemical one.

II. INVESTIGATION OF METHODS OF ANALYSIS

1. Method of the investigation

A solution containing known amounts of carefully purified salts of lead, thorium, and uranium was made up and analysed. The results of these analyses should be a measure of the accuracy of the methods employed. The most accurate methods were finally applied to the analysis of Spruce Pine, North Carolina, uraninite.

2. Purification of lead

Twenty grams of reagent grade lead nitrate were dissolved in hot water and evaporated in a pyrex dish until the solution was saturated. The addition of 5 ml of nitric acid produced a white precipitate because of the greater insolubility of the salt in this acid. This precipitate was filtered and washed with concentrated nitric acid; it was then dissolved in hot water and the above process repeated. The precipitate was again dissolved in hot water and the above process repeated. The precipitate was again dissolved in hot water and the solution evaporated until saturated. The dish was chilled with ice and the resulting crystals were transferred to a filter, washed with a small quantity of ice water, and finally dissolved by

pouring hot water through the filter. This solution was evaporated and crystals obtained twice more in the same manner. The mother liquor in each case was discarded.

The lead nitrate thus obtained by two crystallizations from nitric acid and three crystallizations from water was dried on filter paper, transferred to a weighing bottle, and dried in the oven at 120° C for two hours. The weighing bottle was kept in a dessicator for six weeks. A sample weighing 2.15469 grams was then weighed by difference and transferred to a calibrated 500 ml volumetric flask.

3. Purification of sebacid acid

Twenty grams of sebacic acid were dissolved in water and alcohol and filtered twice. The solution was diluted to 800 ml and heated to boiling. Sebacic acid is soluble in very hot water but almost insoluble in cold water. It was necessary therefore to keep the solution hot during filtration. This was accomplished by filtering the almost boiling solution from a one liter Erlenmeyer flask into another liter Erlenmeyer flask in which 100 ml of water were boiling at the beginning of the filtration. The filtrate was kept at the boiling point during the procedure. A pyrex funnel was used.

The sebacid acid separated out when the filtrate cool-

ed. This precipitate was washed several times by decantation. It was then filtered and the washing continued on the filter. The precipitate was then dissolved again in boiling water; the solution was filtered hot as before; and the sebacic acid recovered by cooling the filtrate. This procedure of solution, filtration, and crystallization was repeated for the third time.

A second quantity of sebacic acid weighing about 100 grams was then purified in the same way except that a hot water funnel was used for the filtration.

4. Purification of thorium

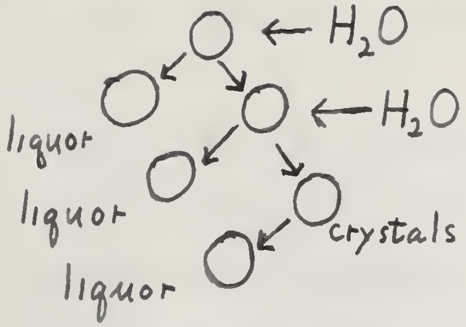
Thirty grams of thorium nitrate were dissolved in 200 ml of distilled water, made 0.3 normal in hydrochloric acid, and treated with hydrogen sulfide for twenty minutes in the cold and then for thirty minutes at the boiling point. The solution was cooled and filtered. The filtrate was boiled to expel the hydrogen sulfide. To the solution, after cooling, were added 10 ml of nitric acid and then a solution of ammonia saturated with ammonium carbonate until the odor of ammonia was distinctly noticeable. A copious white precipitate was obtained. This precipitate was dissolved in excess ammonium carbonate solution and filtered. Nitric acid was added to the filtrate and the

solution was boiled to expel the carbon dioxide. Thorium hydroxide was then precipitated with ammonia. This precipitate was filtered and washed. It was then dissolved by pouring nitric acid through the filter and the entire solution was refiltered. The solution was evaporated to dryness several times on the steam bath to expel the excess nitric acid since a neutral solution of thorium nitrate was desired.

The slightly acid solution finally obtained was heated to boiling and treated with a boiling solution of the sebacic acid purified as above. A white precipitate of thorium sebacate formed.

The precipitate was filtered hot and washed with hot water to remove the excess sebacic acid. The precipitate was then removed to a liter beaker, boiled with 800 ml of water, again filtered hot, and finally washed with hot water. The thorium sebacate was then boiled with excess nitric acid; on cooling, thorium nitrate remained in solution, while sebacic acid precipitated. The precipitate was again boiled with nitric acid. The two filtrates containing thorium nitrate were united and treated with ammonia. The precipitate of thorium hydroxide was filtered, washed, dissolved in nitric acid, and crystallized.

The crystals were recrystallized three times. The final crystals were dissolved in water and reserved for



the sample. The three liquors were united and diluted to 300 ml and the thorium precipitated with ammonia. This precipitate was dissolved in nitric acid, evaporated to dryness several times on the steam bath, dissolved in water, and treated with the sebacic acid recovered above. The thorium sebacate was converted to thorium nitrate and the thorium nitrate was recrystallized three times in the same manner as before. The final crop of crystals was added to the solution reserved for the sample; the mother liquors were discarded. The solution of thorium nitrate obtained was then analysed to determine its concentration.

The solution was thoroughly shaken in a volumetric flask. A weight buret was repeatedly filled and allowed to drain back into the volumetric flask with thorough shaking each time. Samples weighing 72.7744 grams, 71.5400 grams, and 19.6516 grams (a total of 163.9660 grams) were transferred to the volumetric flask which was to contain the standard sample and six samples for analysis were weighed. The weight in vacuum of the

thorium solution is 164.1398 grams. The weights of the six samples chosen for analysis were also reduced to vacuum.

Samples 1 - 3, diluted to 200 ml, were heated to about 60° C and poured into 600 ml beakers containing 100 ml of 10 % oxalic acid solution. The precipitates were allowed to stand twelve hours at room temperature, then digested for twenty-four hours on the steam bath. Later experimental results would indicate that this is not long enough for a precipitate of thorium oxalate to form completely. The precipitates were collected on # 42 Whatman paper, washed with 2 % oxalic acid solution, and ignited to constant weight as ThO_2 in vitrosil crucibles.

Samples 4 - 6 were diluted to 200 ml and treated with 10 ml of freshly distilled ammonia. The precipitates were allowed to stand over night, filtered onto # 40 Whatman paper, washed with 1 % ammonium nitrate, and ignited to constant weight as ThO_2 in vitrosil crucibles.

Sample number	Weight of sample	Weight of precipitate	Per cent of thorium
1.	11.6471	0.14312	1.080
2.	10.8765	0.13441	1.086
3.	12.4456	0.15343	1.084
4.	11.6102	0.14412	1.091
5.	12.7636	0.15839	1.091
6.	11.0930	0.13755	1.090

The average of these six determinations is 1.087 %. This indicates that the solution contains 1.7842 grams of thorium in a total volume of 500 ml. Each 25 ml sample therefore will contain 0.08921 grams of thorium and the precipitate of thorium dioxide should weigh 0.1015 grams.

5. Purification of uranium

One hundred grams of uranyl nitrate, $UO_2(NO_3)_2 \cdot 6\ H_2O$, were dissolved in water, filtered, and precipitated with freshly distilled ammonia. The voluminous yellow precipitate was washed three times by decantation, filtered, washed on the filter, and finally dissolved by pouring dilute nitric acid through the filter. Oxalic acid (10 %) was added to the filtrate to precipitate any thorium or rare earths. The solution was filtered and the precipitate discarded.

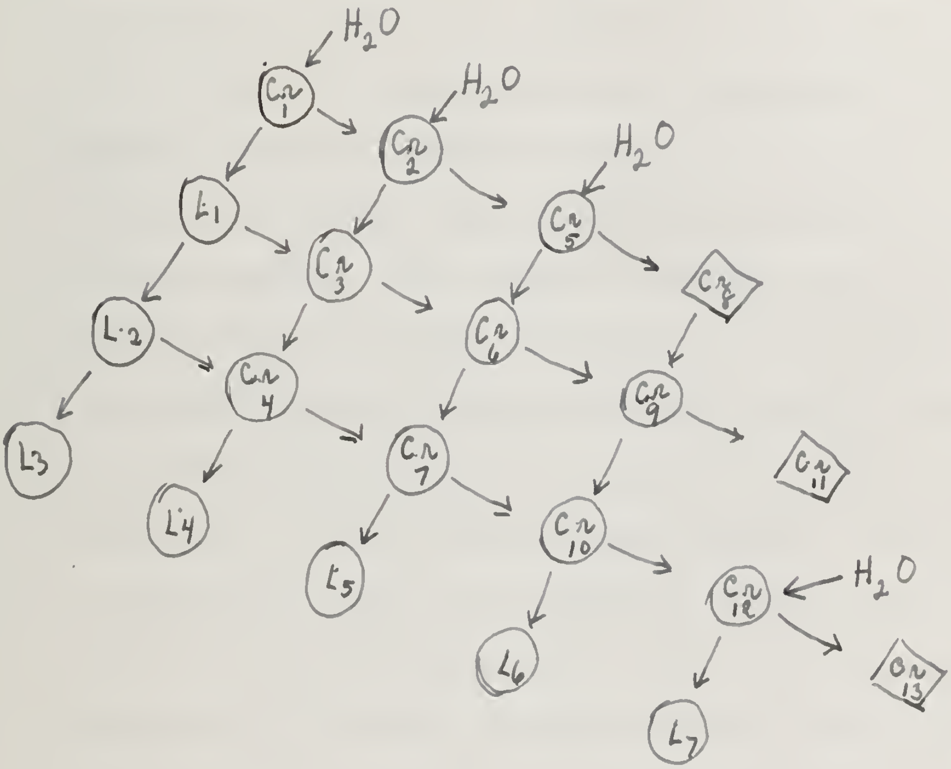
The filtrate was treated with ammonia and the precipitate filtered and washed. It was then dissolved in nitric acid and the solution evaporated to dryness. The crystals were dissolved in water and treated with a solution of ammonia saturated with ammonium carbonate. Even when solid ammonium carbonate was added, there was considerable yellow residue, due probably to the concentration. This treatment should precipitate thorium as carbonate, but hold the uranium in solution. This solution was allowed to stand over night and was then filtered. The filtrate

was boiled to expel carbon dioxide. As the boiling progressed, a yellow precipitate separated out. This precipitate was filtered off, dissolved in nitric acid, and reprecipitated with ammonia. This precipitate was also filtered and dissolved in nitric acid. The solution was then evaporated to the point of saturation and allowed to cool. The crystals which separated were set aside.

The mother liquor was added to the residue not dissolved by ammonium carbonate. Nitric acid was added, the solution boiled to expel carbon dioxide, and the uranium precipitated with ammonia. This precipitate was dissolved in nitric acid and treated, a little at a time, with ammonium carbonate solution. The residue was discarded; the filtrates united and boiled. The precipitates which separated on boiling were filtered, washed, dissolved in nitric acid and crystallized. The mother liquor was discarded and the crystals united with those previously obtained.

The entire crop of crystals was now recrystallized according to the chart given below. The final liquors were discarded and crystals 8, 11, and 13 were united. These crystals were dissolved in water, precipitated with ammonia, and the precipitate ignited in small lots in platinum crucibles. Finally all the U_3O_8 thus obtained was placed in a platinum crucible and heated to constant weight. Then 9.6078 grams of the oxide were weighed by

difference from the platinum crucible, dissolved in nitric acid, and added to the standard sample in the 500 ml volumetric flask.



6. Preparation of the standard sample

The mixture of lead nitrate, thorium nitrate, and uranyl nitrate referred to above was diluted almost to 500 ml in a calibrated volumetric flask. The flask was placed in a thermostat at 20° C and diluted to the mark. The sample now contained 2.15469 grams of lead nitrate, $Pb(NO_3)_2$, 1.7842 grams of thorium, and 9.6078 grams of uranium oxide, U_3O_8.

7. Analysis of the prepared sample

The solution prepared as described above was brought to 20° C in a thermostat. Samples were removed with a calibrated 25 ml pipette and placed in liter Erlenmeyer flasks. Each sample was then treated with hydrogen sulfide by the pressure method for three hours in the cold, heated to boiling, and again saturated with hydrogen sulfide for fifteen minutes. The solution was allowed to cool over night and filtered into another liter Erlenmeyer flask. The precipitate was washed as completely as possible into a pyrex evaporating dish. The paper and any particles still adhering to it were ignited in a vitrosil crucible. The ash was dissolved in 1:1 nitric acid and the solution added to the evaporating dish. The flask in which the precipitation had been carried out was then washed thoroughly with dilute nitric acid and this solution also added to the evaporating dish.

The filtrate was then returned to the precipitation flask and the whole process repeated. After the precipitation flask had been cleaned as completely as possible by nitric acid and by washing, the inside of the flask was wiped with a piece of filter paper twisted around a long glass rod. This filter paper was ignited along with the paper through which the final filtration had been made. The same crucible was used for both ignitions. The ash was extracted with nitric acid as before, and the

crucible was thoroughly washed. The solution and washings were added to the evaporating dish.

These combined solutions in the evaporating dish should contain all of the lead. They were evaporated slowly with concentrated nitric acid almost to dryness. The residue was dissolved in water and filtered. The filter paper and the precipitated sulfur were ignited in the same crucible previously used, extracted with nitric acid as before, and the solution added to the filtrate. The solution was now evaporated to dryness, treated with 3 ml of concentrated nitric acid, and dissolved in 50 ml of water. An excess of dilute sulfuric acid was then added and the solution evaporated to fumes of sulfur trioxide. The solution was cooled, treated with 40 ml of water, and allowed to stand over night. The lead was transformed by this process into lead sulfate, which was visible as a white crystalline precipitate at the bottom of the evaporating dish.

This lead sulfate could be filtered through a Gooch crucible and heated to constant weight. This method is not suitable for exact work, however, because of the slight solubility of lead sulfate. Some would remain in the filtrate and more might dissolve on washing. A saturated solution of lead sulfate is frequently used for washing, but this may introduce an error due to evaporation of the solvent during the process.

It was therefore decided to transfer the precipitate and the supernatant liquid to a weighed platinum crucible, fume off the sulfuric acid, and heat the lead sulfate to constant weight. A great deal of difficulty was experienced in this operation. Because of the small volume of the crucible, it is not easy to wash the precipitate into it from the evaporating dish. Furthermore, if water is used to wash the last of the precipitate into the hot concentrated sulfuric acid solution in the crucible, bad spattering results. It is therefore necessary to evaporate each portion entirely to dryness before adding the next.

The greatest source of error, however, is the tendency of the precipitate to creep over the top of the crucible during the evaporation. It was finally discovered that if the crucible were supported on a clay triangle in a porcelain evaporating dish and heated not only by a low flame underneath but also by a hot flame above, the creeping was entirely eliminated. The heating from above was obtained by supporting a Tirrell burner horizontally on a ring stand and directing the full flame across the top of the crucible. Care must be taken that the reducing flame does not come in contact with the platinum. Particles of carbon may get into the crucible during the heating, but they burn away later.

After all the precipitate had been transferred to the crucible and the solution evaporated to dryness, the crucible was heated in the air bath over the full heat of a Meker burner. If there is an air space of 10 - 15 mm between the porcelain evaporating dish and the bottom of the crucible, the temperature inside the crucible does not go high enough to decompose the lead sulfate.

The precipitate of lead sulfate obtained from the solution used should have weighed 0.0985 grams. The first eight samples gave low results due to spattering or creeping as discussed above. Only three of them were weighed as the errors were obvious. After the introduction of the overhead flame the results were slightly high. There are two possible reasons for this: first, the weights include the ash of from five to nine pieces of filter paper used in filtering off the precipitate and in cleaning the precipitation flask; second, the nitric acid extraction of the vitrosil crucible may remove silica.

The filtrate from the lead precipitation was evaporated to dryness on the steam bath or over the low heat of the hot plate. Then 4 ml of nitric acid and a little water were added to dissolve the residue. The solution was diluted to about 600 ml and 100 ml of a saturated solution of oxalic acid were added. The solution was digested on the hot plate for at least twenty-four hours and then allowed to stand at room temperature for one or more days.

The precipitate of thorium oxalate was filtered (Whatman # 42), washed with 4 % oxalic acid solution, and ignited to constant weight as ThO_2.

Since the amount of thorium present in the standard solution rests on an analysis, it is difficult to state just what this precipitate should weigh; but on the basis of an average of the results of the analyses, the precipitate should weigh about 0.1015 grams. The results obtained are very near this figure, the most reliable being about one milligram low. The results indicate that the complete precipitation requires about six days.

The filtrate containing the uranium was evaporated with nitric acid to destroy the oxalic acid. This was first done in a liter beaker covered by a watch glass, but because of the spattering towards the end of the process, subsequent evaporations were conducted in a liter Erlenmeyer flask. The solution was reduced to a volume of about 150 ml on the hot plate and 50 ml of nitric acid were added. Evaporation was then continued until the volume was about 50 ml. Another 50 ml of nitric acid were then added and the process continued until the absence of red fumes and the clear yellow color of the solution indicated that the oxalic acid had been entirely destroyed.

The solution was then evaporated to dryness two or three times with water to destroy the excess of nitric acid and the uranium precipitated by freshly distilled

ammonia. Unless the precipitate is filtered as quickly as possible while still hot, some uranium will go into the filtrate due to the solubility of uranyl hydroxide in the ammonium carbonate formed by the action of the carbon dioxide of the air. It is always necessary to recover uranium from the filtrate by evaporating it to dryness with nitric acid to destroy ammonium salts and then precipitating the uranium with ammonia as before. It is sometimes necessary to repeat this process a third time. Whatman #40 filter paper is satisfactory. The precipitates were washed with 2 % ammonium nitrate solution.

The papers and precipitates were first dried by placing the crucible in a porcelain evaporating dish as a radiator over a low flame. The temperature was then raised and the paper burned off at a low temperature. The residues were then ignited, first with the full heat of a Tirrell burner, and finally with the full heat of a Meker burner to constant weight.

Vitrosil crucibles were used in the first ignitions. Platinum crucibles were then substituted in the hope that the higher temperature possible with platinum might remove the specks of yellow noticed on the top of the ignited residue. This hope was not realized. Eventually vitrosil crucibles were again used because of the fear that reducing gases might go through the platinum and reduce the uranium oxide. It is almost impossible to remove

the last trace of yellow from the precipitates.

If, after ignition to U_3O_8, the residue is dissolved in a few drops of nitric acid and again heated, a uniform gray residue is obtained, but the process is unsatisfactory because the green crystals of uranyl nitrate decompose violently and spatter tiny particles of the uranium compound out of the crucible.

The residue of uranium oxide after ignition should weigh 0.4797. The results were, in general, high. The weights in Table I which are marked with an asterisk,*, were obtained after the addition of nitric acid and indicate the losses which may be expected from decrepitation.

8. Calculation of the weights of the precipitates expected

Volume of the flask containing the sample 499.92 ml

Volume of the pipette used to withdraw samples 24.96 ml

Ratio of the volume of the pipette to the volume of the flask 0.048791

Lead: (Weight of lead nitrate) x (factor $PbSO_4/Pb(NO_3)_2$) x 0.048791 = 2.15469 x 303.270/331.226 x 0.048791 = 0.09850 grams.

Thorium: (Weight of solution) x (per cent thorium) x (factor ThO_2/Th) x 0.048791 = 164.140 x 0.01087 x 264.12/232.12 x 0.048791 = 0.1015 grams

Uranium : Weight of U_3O_8 x 0.048791 =

9.6078 x 0.048791 = 0.4797 grams.

Table I

Summary of the results on the preliminary solution

	Lead	Thorium		Uranium
	$PbSO_4$	ThO_2		U_3O_8
	Precipitates should weigh (calculated)			
	0.09850	0.1015		0.4797
	The weights actually obtained were:			
1.		0.1008		0.4925
2.				
3.				0.4978
4.	0.0841	0.1017		0.4846
5.	0.0752	0.1018		0.4817 *
6.		0.1019		0.4666 *
7.	0.0847	0.1012		0.4845
8.		0.1009		0.4838
9.	0.1059	0.0991	(48 hours)	0.4816*
10.	0.1033	0.0991	"	0.4800 *
11.	0.1041	0.0991	"	
12.	0.1026	0.0991	"	
13.	0.1037	0.1006	(72 hours)	
14.	0.1027	0.0999	"	
15.	0.1007			
16.		0.1005	(6 days)	
17.	0.0995	0.1006	"	

A new sample

1. Preparation of a new sample

In order to study the methods of analysis further, a new sample was made up. The same lead nitrate which was used for the first sample was dried for two hours at 120° C and cooled over night in a dessicator. A sample weighing 1.31248 grams was weighed out on to a tared watch glass.

A new thorium sample was purified as before, but with the added care that the previous experience made possible. Two separations as thorium sebacate were made. The final purified precipitate of thorium hydroxide was dissolved in the least possible amount of nitric acid so that the solution was practically neutral. A sample of this thorium solution weighing 43.6801 grams in air (43.7264 grams in vacuum) was weighed from a weight buret.

The uranium oxide purified for the first sample was dissolved in nitric acid, precipitated with freshly distilled ammonia, dissolved in the least possible amount of nitric acid, and crystallized three times from water. It was then dissolved in water, precipitated as uranyl hydroxide, and ignited in small quantities to U_3O_8. A sample weighing 9.91163 grams was then weighed by difference from the platinum crucible in which the ignition had been carried out.

The lead nitrate, the thorium nitrate solution, and

the uranium oxide dissolved in the least possible amount of nitric acid were added to a calibrated liter volumetric flask and diluted to the mark in a thermostat at 20° C.

Four samples of the purified thorium solution were weighed out and analyzed to determine its strength. Samples (1) and (2) were evaporated to dryness in vitrosil crucibles on the steam bath and carefully ignited to thorium dioxide. Sample (3) was weighed into a 250 ml beaker, diluted to 100 ml, and treated with 50 ml of a solution containing 10 ml of freshly distilled ammonia. The precipitate was digested on the steam bath for an hour, allowed to stand over night, and filtered. Sample (4) was weighed into a 250 ml beaker and diluted to 100 ml. It was then added to 500 ml of boiling 20 % oxalic acid solution and 200 ml of water added. The resulting mixture was kept on the low heat of the hot plate for three days, allowed to cool over night, and filtered. The precipitates were ignited to constant weight and the per cent of thorium dioxide computed.

	Weight of the sample (vacuum)	Weight of the precipitate	Per cent of thorium dioxide
1.	10.3647	0.24432	2.357 %
2.	17.0091	0.40032	2.354 %
3.	12.2115	0.28800	2.358 %
4.	11.4881	0.27101	2.358 %

2. Calculation of the results to be expected in the analyses

Volume of the volumetric flask	1000.29 ml
Volume of the pipette used to withdraw samples	49.91 ml

For purposes of the calculation it is assumed that 49.91 ml of the standard solution represents a 0.7000 gram sample of a radioactive mineral. The percentages of lead, thorium, and uranium to be expected are then determined as shown below.

Lead: (Weight of lead nitrate) x (factor $Pb/Pb(NO_3)_2$) x (1/0.7000) x (49.91/1000.29)

$$\frac{1.31248 \times 207.21 \times 49.91}{331.226 \times 0.7000 \times 1000.29} = 5.853\ \%$$

Thorium: (Weight of thorium dioxide) x (factor Th/ThO_2) x (1/0.7000) x (49.91 x 1000.29)

$$\frac{43.7264 \times 2.357 \times 232.12 \times 49.91}{100 \times 264.12 \times 0.7000 \times 1000.29} = 6.456\ \%$$

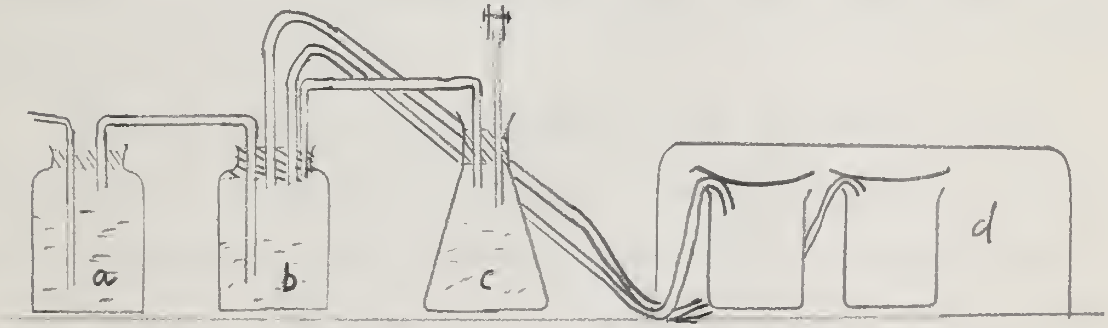
Uranium: (Weight of uranium oxide) x (factor $3\ U/U_3O_8$) x (1/0.7000) x (49.91/1000.29

$$\frac{9.91193 \times 3 \times 238.07 \times 49.91}{842.21 \times 0.7000 \times 1000.29} = 59.913\ \%$$

Investigation of the methods for the determination of lead

1. Separation of lead as sulfide as sulfide and determination as sulfate

The acid concentration of the standard solution was determined by titrating a 25 ml sample with standard NaOH. This titration indicated that the solution contained about 1 % of nitric acid. A 50 ml sample was taken by a pipette at 20° C and placed in a 600 ml beaker. The sample was first heated on the hot plate almost to boiling and then placed in the hydrogen sulfide apparatus shown below.



Hydrogen sulfide from an iron sulfide - hydrochloric acid generator is led through the two wash bottles, a and b. From b two delivery tubes carry hydrogen sulfide to the tops of two beakers under an inverted battery jar

and another delivery tube carries the gas into a liter Erlenmeyer flask containing distilled water for use in washing the precipitated sulfides later. The hydrogen sulfide fills the beakers and displaces the air by gravity.

Hydrogen sulfide was passed in for two hours - not continuously, but a little at a time so that the apparatus was always full of gas. The solution was left in the apparatus over night. In the morning it was filtered into a 600 ml beaker (Whatman # 40) and the precipitate was well washed with hydrogen sulfide water. Complete removal of the precipitate from the precipitation beaker is unnecessary as long as it is well washed. After washing, the paper containing the precipitate was removed from the funnel and dropped into the precipitation beaker. This beaker was then covered and set aside.

To the filtrate, which had a volume of about 250 ml, were added 2 ml of nitric acid. It was then heated, treated with hydrogen sulfide for three hours, and filtered into a liter beaker. The paper was thoroughly washed with hydrogen sulfide water. The first precipitation was almost always complete as shown by the fact that the second filter paper was usually pure white. In only a few cases was the paper colored at all by the precipitate and then only to a very slight extent.

The filtrate was then placed on the low heat of the

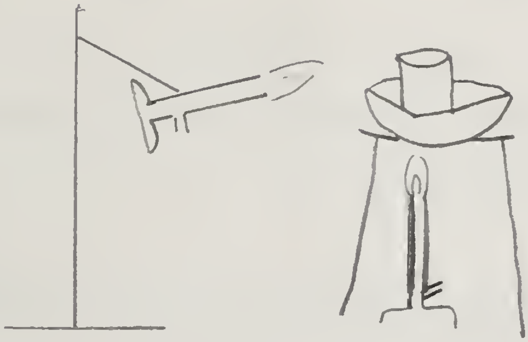
hot plate over night to expel hydrogen sulfide and was then analyzed for thorium and uranium as described below.

The filter paper containing the second precipitate of lead sulfide was also dropped into the first precipitation beaker. To this beaker 5 ml of nitric acid were added and the sides were washed down by a stream from the wash bottle. The paper and the precipitate were digested on the hot plate with frequent stirring. Dilute (1:10) nitric acid was added from time to time. When the precipitate was dissolved and the paper was entirely disintegrated, the solution was cooled, diluted to 50 ml, and filtered. The residue on the filter paper was thoroughly washed with hot water. All the lead should be washed out of the paper by this process. The paper was then burned in a weighed platinum crucible and ignited to ash.

The filtrate which contained the lead nitrate in a volume of about 100 ml was evaporated to about 50 ml and a small portion then poured into the platinum crucible. The solution in the platinum crucible was then evaporated to dryness in an air bath arranged as follows:

A porcelain evaporating dish was supported on a tripod. Suspended in it by a quartz covered triangle was the platinum crucible. The low flame of the Tirrell burner heated the evaporating dish from beneath. The full flame of another Tirrell burner suppotted on a ring stand was directed above

and to one side of the crucible as shown in the diagram.



More of the solution was added to the crucible from time to time as the evaporation progressed. Eventually all of the nitric acid was volatilized and white crystals of lead nitrate were formed. Then the crucible was almost filled with dilute sulfuric acid and this was evaporated to dryness. Finally one drop of concentrated sulfuric acid was added and fumed off. The residue, when perfectly dry, was heated with a Meker burner underneath the evaporating dish. One more drop of sulfuric acid was added and the crucible heated as before. When all the particles of carbon which apparently were absorbed from the gas flame were burned off and the residue appeared pure white, the crucible was cooled and weighed.

	(21)	(22)
Weight of lead sulfate	0.05966	0.05981
Per cent of lead	5.823 %	5.838 %

Mean: 5.830 %; deviation from the mean: 1.37 parts/1000

Theoretical: 5.853 %; deviation from the theoretical:
3.9 parts/1000 (low)

It is obvious from these results that this method, with care, can give results not far from the correct value. It was decided, therefore, to leave this method for a time and examine the molybdate and chromate methods.

2. The determination of lead as molybdate

The solution of lead nitrate was prepared as before. The final residue of filter paper which should contain no lead or only the slightest traces was ignited in a weighed vitrosil crucible. The ash was treated with one drop of nitric acid and a few drops of water. After digesting for fifteen minutes on the hot plate, the solution was washed into the main solution in the beaker and the crucible set aside for the ignition of the lead precipitate.

The solution of lead nitrate was heated to boiling and kept hot on the hot plate while a 2.5 % solution of ammonium molybdate was added dropwise from a buret. When precipitation appeared to be complete, the precipitate was allowed to settle and another drop of the precipitant added.

Dilute ammonia was then added from a buret to a methyl orange end point. The solution was then acidified with acetic acid and the precipitate filtered through Whatman # 42 filter paper. The precipitate was washed with hot 2 % ammonium nitrate solution. The paper without removal from the funnel was carefully dried in an air bath. It was then removed and ignited in the vitrosil crucibles referred to above. One of the precipitates melted into a small globule (apparently lead), but the other gave the following results:

Weight of $PbMoO_4$	0.07272 g
Per cent of lead	5.863 %
Theoretical	5.853 %

Deviation from the theoretical: 1.7 parts/ 1000 (high)

Two more samples of lead nitrate were prepared in exactly the same way as before. Then 50 ml of 50 % ammonium acetate solution were added and the solution was diluted to 200 ml. It was then heated to boiling and exactly 2.5 ml of 2.5 % ammonium molybdate solution were added dropwise from a buret to the acid solution. Then 5 ml of ammonia were added and the precipitate allowed to digest one hour on the hot plate.

The precipitates were filtered through Whatman # 42 filter paper and washed with hot 2 % ammonium nitrate solution as before. The paper, without drying, was placed

in weighed vitrosil crucibles, dried very slowly in an evaporating dish as a radiator, and ignited in the usual manner. Since the paper did not seem entirely converted to ash even after three heatings, a drop of nitric acid was added and the crucible heated again.

Weight of $PbMoO_4$	0.07209	0.07194
Per cent lead	5.812	5.800

Deviation from the mean: 1 part / 970

Deviation of the mean from the theoretical: 8 parts/ 1000 (low)

Two more precipitates of lead molybdate were prepared in exactly the same way as before. They were filtered by suction through sintered glass crucibles and washed with hot ammonium nitrate solution (2 %). The crucibles were dried in an oven at 150° C for three hours. They were then heated in an air bath at 240° C and weighed. Finally they were heated two hours more at 280° C and again weighed.

After heating at 240°C	0.07496	0.07326
After heating at 280° C	0.07452	0.07294
Per cent of lead	6.033 %	5.973 %

Deviation of the mean: 5 parts/1000

Deviation of the mean from the theoretical: 25 parts/1000

With the solution buffered as above, the precipitation is very satisfactory. The precipitate is coarse and filters easily. If it could be ignited satisfactorily, this would be a very good method for lead. One of the first ignitions made with paper was obviously reduced. When the solution was buffered with ammonium acetate, however, the results were very good.

The results obtained by the use of sintered glass crucibles was too high. It is obvious that a temperature higher than 280° C must be used in order to volatilize the ammonium nitrate contained in the wash water, and higher temperatures are not desirable with this type of crucible. Gooch crucibles might be used, but were not considered exact enough for this work.

The indication that the molybdate method would be accurate if a buffer were used was later confirmed by Sterling and Spuhr[1]. They also found that[2] a "heavy semi-metallic sintered product" was obtained in early experiments. They attributed this to hydrolysis and stated [2] that "increasing the amount of ammonium chloride in the solution overcame the difficulty".

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[1] Ind. and Eng. Chem., Anal. Ed., January 1940, page 33

[2] Private communication from C. Sterling

3. The determination of lead as chromate

Solutions of lead nitrate were prepared as before and evaporated to dryness. Then 150 ml of water and 1 ml of nitric acid were added. The solution was heated on the hot plate and 5 ml of 5 % ammonium chromate were added dropwise from a pipette. Precipitates formed in all but one of the first four samples. This sample had not been evaporated to complete dryness, but it had been carried to a point where the bottom of the beaker was barely moist. The addition of 15 ml of dilute ammonia was necessary to bring down this precipitate. Apparently the pH is more important in this determination than the textbooks indicate.

The first two samples were filtered through No. 3 sintered glass crucibles; the other two were digested over the week end on the low heat of an electric hot plate. The two which were filtered immediately ran through the filter. The first one apparently was retained on the second filtration, but the second ran through the filter so badly even on the second filtration that it was discarded.

The two solutions which digested over the week end turned green and were discarded.

The one precipitate which was obtained from this set (# 31) weighed 0.05895 grams. This corresponds to 5.398 % of lead.

Two more lead solutions (35 and 36) were prepared as before. They were diluted to 100 ml and neutralized with dilute ammonia until a precipitate just formed. This precipitate was dissolved in 1.5 N nitric acid and 2 ml excess were added. Then 10 ml of 5 % ammonium chromate were added slowly from a pipette. The precipitates were digested on the hot plate over night. The solutions were cooled and filtered through weighed sintered glass crucibles. One of the precipitates (36) seemed to be completely retained by the filter; the other had to be refiltered. The precipitate was washed first with dilute ammonium chromate and then with alcohol.

On the basis of a 0.7000 gram sample, the results were 5.66 % and 5.78 %. The mean was 5.72 %; the deviation from the mean was 10 parts / 1000; and the deviation of the mean from the theoretical was 22 parts / 1000 low.

The precipitation and filtration of lead as chromate is less satisfactory than as molybdate. Not only must the pH of the solution be carefully controlled, but also the greatest care must be exercised in filtration.

While undoubtedly better results could be obtained with practise, enough has been done to show that either the lead sulfate method or the lead molybdate method should be used.

Investigation of the methods for the determination of thorium

1. Separation of thorium as oxalate

The filtrate from which the lead had been removed was evaporated in a liter beaker until the odor of hydrogen sulfide could no longer be detected. The solution was diluted to 600 ml and 100 ml of saturated oxalic acid added.

Samples 21 and 22 were allowed to stand on the hot plate for 24 hours and then filtered through Whatman # 40 filter paper. The precipitate was washed with 2-3 % oxalic acid solution, ignited, and weighed. The results were 5.67 % and 6.12 %, with the mean 5.94 %. The deviation from the mean was 45 parts / 1000; the deviation of the mean from the theoretical was 83 parts / 1000 low.

These results were much too low, probably because 24 hours is not long enough for the precipitate to form.

Samples 23 and 24 were treated in the same way except that the precipitates were allowed to digest 48 hours on the hot plate and three days more at room temperature.

Samples 25 - 28 were carefully evaporated just to dryness on the hot plate. About 100 ml of water were added and the evaporation was repeated to expel all the nitric acid. The solution was then diluted to 700 ml. To samples 25 and 26 were added 10 ml of concentrated HCl; to samples

27 and 28 were added 5 ml of concentrated HCl. Then the solutions were heated just to boiling on the hot plate and 100 ml of concentrated oxalic acid were added. The solutions were kept on the hot plate for 48 hours and allowed to evaporate down to a volume of about 400 ml.

The ignited precipitate of # 28 had a pronounced yellow color. This might have been due to uranium, but it is hard to understand why uranium should not have been present as the gray U_3O_8. It could not have been due to rare earths because the original thorium solution when evaporated to dryness gave pure white residues. Since this precipitate was obviously contaminated, it was discarded.

These thorium separations gave the following results:

	Digested on hot plate	Digested at room temperature	HCl present
21. 5.67 %	24 hours		
22. 6.21 %	24 hours		
23. 6.257 %	48 hours	3 days	
24. 6.256 %	48 hours	3 days	
25. 6.305 %	48 hours		1 %
26. 6.316 %	48 hours		1 %
27. 6.279 %	48 hours		½ %
Theoretical	6.456 %		

2. Thorium as sebacate

a. Preliminary experiments

Thorium oxalate was precipitated and filtered as for samples 25 and 26. The well washed precipitate and the filter paper were placed in a 400 ml beaker and 20 ml of 1-1 nitric acid added. The mixture was digested three hours on the hot plate with frequent stirring. Dilute nitric acid (1-10) was added from time to time to replace the liquid lost by evaporation. Finally the solution was allowed to evaporate almost to dryness to expel excess acid and 100 ml of water were added. The solution was allowed to digest on the hot plate for one hour and then cooled to room temperature. The nitric acid still remaining was then neutralized with dilute ammonia. The solution was left just on the acid side to methyl red, but with no excess acid.

The solution was heated to boiling and a boiling solution of sebacic acid added in excess. The mixture was allowed to stand about fifteen minutes and filtered (# 40 paper). The precipitate was washed with hot water. An excess of sebacic acid was indeed present as shown by the fact that it dissolved on the filter in the hot wash water and recrystallized in the filtrate on cooling.

The precipitate was ignited first at how heat, but finally for four hours over a Meker burner. The four precipitates obtained from samples 29 - 32 had the following

weights: 0.05142 g, 0.01654 g, 0.05052 g, and 0.01541 g.

By chance the first precipitate weighs exactly what it should, but there is no agreement whatever among the weights. Some unknown factor has obviously entered to upset this determination. An attempt was made to discover the nature of this unknown factor.

The thorium in samples 33 - 36 was precipitated as oxalate, filtered, and washed as before. The filter paper and the precipitate were then digested for one hour on the hot plate with 10 ml of nitric acid and small quantities of water. The solution was then diluted to 100 ml, heated to boiling and filtered. The residue was well washed with hot water and ignited. The weights of the ignited residues, which should not have exceeded the weights of filter paper ash, were: 0.05002 g, 0.04914 g, 0.04727 g, and 0.04725 g.

The filtrates were evaporated to dryness three times to expel nitric acid and then were diluted to 100 ml. To the solutions were added 2 or 3 ml of 1-10 HCl and sebacic acid as above. The precipitates were ignited in the same crucibles as before. The weights of the combined residues were: 0.05009 g, 0.04949 g, 0.05032 g, and 0.05017 g.

If the percentages of thorium in the assumed sample (0.7000 g) are figured from these data, the results are: 6.289 %, 6.213 %, 6.318 %, and 6.299 %.

Now the purpose of dissolving the thorium oxalate

in nitric acid and reprecipitating it as thorium sebacate is to separate it from the rare earths, since the oxalates of the rare earths are insoluble while their sebacates are soluble. In a regular analysis, therefore, the nitric acid solution would be filtered, the residue well washed and discarded, and the filtrate treated with sebacic acid. If that procedure had been followed here, however, practically all of the thorium would have been discarded and the results would have been much too low. Evidently the solution of the oxalates is not accomplished as easily as has been supposed.

b. Experiments on the solubility of thorium oxalate

In an attempt to investigate the problem further a special solution of thorium nitrate was prepared and 50 ml samples were removed with a pipette. From these solutions thorium oxalate was precipitated as before. The solutions containing the fresh precipitates of thorium oxalate were evaporated on the hot plate to a volume of 400 ml and allowed to stand nine days at room temperature. They were then filtered (# 42) and washed. The precipitates and filter paper were then returned to the precipitation beakers and treated as follows: Numbers 1 and 2: 4 ml HCl and 6 ml HNO_3; numbers 3 and 4: 10 ml HNO_3. An inspection two days later showed no indication that any solution had occurred in the cold acid. The beakers were

then set on the hot plate (low heat) for three hours. Then 6 ml HCl and 4ml HNO_3 were added to numbers 1 and 2, 10 ml HNO_3 were added to numbers 3 and 4, and the digestion was continued for one hour. The solutions were then set aside. No crystalline particles could be seen, but the solutions contained disintegrated filter paper.

After three days the solutions were diluted to 50 ml and filtered immediately. The filter paper was washed ten times with cold water. The filtrates were clear at this time, but when examined two days later showed a fine crystalline precipitate on the bottom of the beaker. These precipitates were also filtered.

If all the thorium oxalate had dissolved in the hot acid, the residues from the ignition of the papers obtained in the first filtration should consist only of ash. These residues, however, weighed 0.01305 g, 0.01361 g, 0.00052 g, and 0.00394 g. Obviously a large amount of thorium oxalate did not dissolve, but the greater solubility of this substance in nitric acid is noticeable.

The precipitates which separated on standing were ignited in the same crucibles with the following results: 0.04946 g, 0.04938 g, 0.06069 g, and 0.05807 g. The total amounts of insoluble residue were 0.06251 g, 0.06299 g, 0.06121 g, and 0.06201 g. These results show that neither aqua regia nor nitric acid can be relied upon to dissolve thorium oxalate.

The solutions from which the insoluble material had been removed were then neutralized with ammonia to a methyl orange end point and then acidified with sebacic acid. The precipitates were heated to boiling, filtered immediately, and washed with hot water. They were then ignited in the proper crucibles. Samples 1 and 2 gave total residues of 0.06300 and 0.06333 grams- an increase of only 0.49 and 0.34 mg separated by the sebacic acid.

Similar samples were precipitated as oxalate, the precipitates filtered, washed, and returned to the precipitation beakers. Samples 5 and 6 were treated with 10 ml HCl; samples 7 and 8, with 10 ml H_2SO_4. They were digested several hours on the hot plate, more acid being added as needed. The solutions were then diluted to 50 ml, filtered, washed with hot water and the residues ignited. The weights of these residues after ignition were 0.06371 g, 0.06384 g, 0.00036 g, and 0.00041 g. The first two results check so well with the total ThO_2 from samples 1 and 2 that it is evident that little, if any, thorium oxalate dissolved in HCl. The amounts undissolved by the sulfuric acid, on the other hand, are very small.

The digestion with concentrated sulfuric acid charred the paper but did not oxidize it to a clear solution. The filter was filled to the brim with the charry mass and some of the thorium may have been retained mechanically. Even so,

after the weight of the filter paper had been deducted, the weight of thorium dioxide did not exceed two or three tenths of a milligram.

The filtrates from samples 7 and 8 were neutralized with dilute ammonia to a methyl orange end point, and a few drops of nitric acid were added to an acid end point. The solution was back titrated with dilute 1-10 ammonia from a buret. Then enough sebacic acid was added to change the color of the indicator back to red. The precipitate was digested on the hot plate over night, filtered, washed with hot water and ignited. The crucibles were weighed to the nearest milligram only since it was evident that the weights did not check (0.011 and 0.024). The precipitation with sebacic acid was obviously not complete.

c. Effect of pH on the precipitation of thorium sebacate

Four 10 ml samples of a thorium nitrate solution were withdrawn by a pipette and placed in 250 ml beakers and heated. Ammonia was added to the first sample, drop by drop, until a cloudiness appeared. This cloudiness was then just cleared with nitric acid. Methyl orange was then added and the solution titrated with ammonia. A precipitate was very evident at the end point. The precipitate did not dissolve when a drop of nitric acid was added and the indicator turned pink. Six more drops of nitric acid were required to

dissolve the precipitate.

The cloudiness produced by ammonia in samples 1 and 2 was just cleared with nitric acid. Sample 3 was titrated with ammonia to a methyl orange end point and ½ ml of concentrated nitric acid added. Sample 4 was titrated as above, and 1 ml of concentrated nitric acid added. Solid sebacic acid was then added to each sample. The precipitates were filtered, washed, and ignited. The weights of the ignited residues were 0.15567 g, 0.16002 g, 0.01448 g, and 0.00209 g. The first two samples should have given residues weighing exactly the same. The data from these experiments are a further example of the extraordinary sensitivity of thorium sebacate to the pH of the solution.

The 10 ml sample of the solution used in these experiments gave a precipitate of 0.16 g of thorium dioxide. Based on calculation from the data above, a new solution of thorium nitrate was made up so that a 50 ml sample should give a precipitate weighing slightly more than 0.008 g.

Two samples (1 and 2) of this new sample were treated with 25 ml of 50 % ammonium acetate solution and 25 ml of water. Two samples (3 and 4) were treated with 50 ml of 50 % ammonium acetate solution. Two samples (5 and 6) were treated with 10 ml of ammonia. Two samples (7 and 8) were neutralized to a methyl orange end point and 50 ml of 50 % ammonium acetate solution were added. A large excess of

sebacic acid was then added to samples 1 and 2; and a slight excess of sebacic acid was added to samples 3,4,7, and 8. Then 5 ml of 1-1 ammonia was added to samples 7 and 8. The sebacic acid was added in solid form to the hot solutions. The precipitates were filtered immediately, washed with hot water and ignited. The results may be seen in the table.

Sample number	Treated with	Precipitant	Weight of precipitate
1	25 ml 50 % NH_4Ac	sebacic acid	0.00492 g
2	"	"	0.00443 g
3	50 ml 50 % NH_4Ac	"	0.00196 g
4	"	"	0.00243 g
5	________________	ammonia	0.01065 g
6	________________	ammonia	0.01063 g
7	(neutral) + 5 ml 1-1 NH_3 and 50 ml 50 % NH_4Ac	sebacic acid	0.00038 g
8	"	"	0.00591 g

It is obvious that the only weights approximating the expected 0.008 g were those obtained by precipitating thorium as hydroxide. The results obtained by using sebacic acid are not dependable at all. The addition of ammonium acetate buffer did not help in any way. After these experiments all attempts to use sebacic acid as a precipitant for thorium were abandoned.

A further discussion of the sebacate method will be found, however, in the account of the analyses of uraninite samples 1 through 6, below. The analyses of these samples was started before the preliminary investigations were entirely finished, so that some experiments might be conducted on actual thorium samples containing rare earths.

3. The determination of thorium as phenylarsonate

Two 50 ml samples of a pure thorium nitrate solution were removed with a pipette and transferred to 600 ml beakers. These samples were heated and treated with 100 ml of 10 % oxalic acid solution as previously described. The precipitate was filtered after five days. One sample was ignited directly to oxide. The other was evaporated with 25 ml of 1-1 nitric acid until brown fumes were no longer evolved and the filter paper was well digested. Then 300 ml of a dilute solution of sulfur dioxide (formed by bubbling the pure gas generated from pure sodium sulfite and pure hydrochloric acid into distilled water) were added and the solution heated to boiling. From this solution the thorium was precipitated by the addition of 30 ml of 10 % phenylarsonic acid, $C_6H_5\ AsO(OH)_2$, solution, 75 ml glacial acetic acid, and 20 ml of 50 % ammonium acetate solution. The mixture was allowed to digest on the hot plate for a few minutes, filtered through #40 Whatman

paper, and the residue washed with a solution made by adding 20 ml of 50 % ammonium acetate solution and 10 ml of acetic acid to 500 ml of distilled water. The precipitate was dissolved in 30 ml of 1-1 HCl by boiling the solution containing the paper and precipitate on the hot plate for about one hour with frequent stirring and the addition of dilute acid to replace that lost by evaporation. The hot solution was filtered and the mass of pulp on the filter was washed thoroughly with hot water.

The filtrate was diluted to 300 ml by the addition of dilute sulfurous acid as before to insure the reduction of cerium (when it is present). The thorium phenylarsonate was then reprecipitated by the addition of 10 ml of 10 % phenylarsonic acid, 75 ml of acetic acid, and 20 ml of 50 % ammonium acetate. This precipitate was filtered, washed, and dissolved in dilute hydrochloric acid as above. The solution, without filtering, was diluted to 300 ml, heated, and treated with 100 ml of 10 % oxalic acid solution.

Since the filtrate from the first separation of thorium phenylarsonate was slightly turbid, it was refiltered through # 42 Whatman paper and the resulting residue treated as above. The two final precipitates of thorium oxalate were ignited separately. The results indicate that this precipitate must be filtered through fine grained paper.

Weight of residue (# 40 paper)	0.00154 g
Weight of residue (# 42 paper)	0.00443 g
Total weight of ThO_2 residue by this method	0.00597 g
Weight of ThO_2 by direct ignition	0.00593 g

Since these data indicate that the phenylarsonic acid separation is satisfactory, thorium samples from the uraninite ore (7 - 15) were put through the process; but, as a further check on the accuracy of the method, four equal samples were removed from a pure thorium nitrate solution of slightly greater concentration than before. These samples were precipitated as oxalate. Two of the precipitates were ignited directly; and two were put through the phenylarsonic acid separation process described above. The results indicate that the method is reliable.

Weights by direct ignition	0.0111 g	0.0114 g
Weights after the phenylarsonic acid separation	0.0113 g	0.0113 g

Investigation of the methods for the determination of uranium

The filtrate from the thorium precipitate was received in a liter Erlenmeyer flask. This filtrate was treated with 50 ml of nitric acid and evaporated over the hot plate to about 100 ml. Small amounts of nitric acid were added from time to time and the evaporation continued until the absence of red fumes showed that all the oxalic acid had been destroyed. The solution was then washed into a liter beaker and again evaporated to remove the excess nitric acid. About 200 ml of water were added and the solution heated to boiling. Freshly distilled ammonia was then added to precipitate the uranium and the precipitate was allowed to digest for an hour on the hot plate. It was filtered hot.

The filter paper and the precipitate were removed to a weighed crucible and the funnel rinsed into the filtrate. While practically all the the precipitate had been washed out of the precipitation beaker with 2 % ammonium nitrate solution, no attempt was made to ensure complete removal. The small amount of solid on the walls was dissolved in 10 ml of 1-5 nitric acid. The filtrate and washings were added to this solution and the whole evaporated to dryness two or three times to destroy ammonium salts.

The uranium was recovered from this filtrate by precipitation with ammonia as before in a volume of about 100 ml. The precipitate and filter paper were added to the proper crucible and the process repeated a third time. The precipitates were ignited over the full heat of a Meker burner.

Samples 21 - 24 were treated in this way. The results for samples 21 and 22 were slightly high; but the corresponding thorium results were low. Evidently thorium not removed as oxalate will come down later as hydroxide and cause an error in the uranium determination.

Samples 25 - 28 were also treated in the same way. After the first weighing, a drop of nitric acid was added to each crucible and the crucibles again ignited. Unfortunately, decrepitation occurred so that the results of the first weighing were used to calculate the data shown in the table. These weighings, however, are probably accurate to within 0.2 mg.

Samples 29 - 32 received the same treatment. Samples 31 and 32 showed evidence of incomplete ignition. They contained large masses of yellow and also particles resembling unburned filter paper. This was so evident in the case of sample 32 that the results should be unhesitatingly discarded. The mean of the three remaining samples was 60.19 %, an absolute deviation from the theoretical of 0.26 %. The average deviation from the mean was 13 parts / 1000;

the deviation of the mean from the theoretical was 0.9 parts / 1000.

Samples 33 - 36 stood three months in an Erlenmeyer flask between the time that the thorium was removed and the time that the uranium was precipitated. Since the results were uniformly high, the difference may be due to dissolved silica, especially since the evaporations to dryness to destroy ammonium salts would results in the dehydration of dissolved silica.

Slight traces of yellow always remained after the ignition of the uranium precipitates, although the main bulk of the residue was a dark gray or grayish green. In an attempt to get rid of this, 1 ml of water and 4 drops of nitric acid were added to each crucible containing the residues from samples 33 - 36. Then ammonia was added until a distinct precipitate was obtained. The material in the crucibles was dried carefully in an air bath and ignited. The precipitate showed some tendency to decrepitate, but the crucibles were kept covered throughout.

There still remained some traces of yellow around the edges, so the process was repeated. Spatterings were wiped from the crucible covers with filter paper moistened with dilute nitric acid and returned to the crucibles. Due to the decrepitation, however, the method seems very unsafe. It is more satisfactory to ignite the crucibles for a longer

time.

Some of the yellow flakes from samples 29 - 32 were picked out and ignited in platinum. After ten minutes some of them were red. After one hour, the yellow was as much in evidence as after ten minutes.

Discussion of results

Not all of the results obtained above are valuable for a discussion of the accuracy to be expected in these analyses. Lead results from samples 21, 22, 25, and 26 alone are reliable. The first two of these were obtained by the sulfate method and the second two by the molybdate method. The mean of these four values (5.82, 5.84, 5.81, and 5.80) is 5.82 %. This is only slightly less than the 5.85 % theoretically present.

Thorium results from samples 23, 24, 25, 26, 27, 33, 34, 35, and 36 can be considered. The mean of these nine results is 6.28 %. This is an average deviation from the mean of four parts per thousand, an absolute deviation from the theoretical 6.46 % of 0.18 % low, and a relative deviation from the theoretical of 28 parts / 1000 low.

Uranium results from samples 23, 24, 25, 26, 27, 28, 29, 30, and 31 should be chosen. The mean of these eight results is 60.11 %. The average deviation from the mean is

three parts per thousand, the absolute deviation from the theoretical 59,91 is 0.20 % high, and the relative deviation from the theoretical is three parts per thousand. Since in an actual analysis the silica introduced from the glassware during the procedure would be removed by the filtration of the residue insoluble in ammonia and ammonium carbonate, very accurate results should be expected when the quantities of uranium are as large as in the above cases.

Table II

Summary of the results of the analysis of the second solution

	Per cent of lead	Per cent of thorium	Per cent of uranium
21	5.823 *	5.67	61.16
22	5.838 *	6.21	60.76
23		6.257 *	60.40
24	5.853	6.256 *	60.46
25	5.812 *	6.305 *	59.96 *
26	5.800 *	6.316 *	59.81 *
27		6.279 *	60.16 *
28		6.398	60.11 *
29	6.03		60.06 *
30	5.973		59.91 *
31	5.398		60.61
32			61.26
33		6.289 *	60.89
34		6.213 *	59.89
35	5.66	6.318 *	59.55
36	5.78	6.299 *	61.71

Mean of the starred values

5.82	6.28	60.11

Theoretical values

5.85	6.46	59.91

III. ANALYSIS OF SPRUCE PINE URANINITE

First analysis

The powdered sample as received was ground further in an agate mortar. It was placed in a weighing bottle and dried one hour at 105° C.

Samples of the outside section were weighed into 600 ml beakers and covered with 50 ml 1-1 nitric acid. They were digested six hours on the hot plate, diluted to 200 ml, allowed to stand one week, and filtered. The filtrates were returned to the original beakers and evaporated to dryness. Because of the danger of changing thorium salts to insoluble thoria, the beakers were transferred to the steam bath at the first appearance of red oxide of uranium. Water and nitric acid were added and the solution left on the steam bath for three days. The residue was taken up in 100 ml of dilute nitric acid and filtered. The combined residues from each sample were ignited in platinum and weighed. Three drops of sulfuric acid were added and the crucibles weighed again.

The residues were then treated with sulfuric and hydrofluoric acids, carefully evaporated in an air bath, and finally ignited strongly. The results may be slightly high because of the long treatment before filtering, but this was unavoidable.

The filtrates containing lead, thorium, and uranium were evaporated to dryness on the steam bath to expel all excess nitric acid. Then 100 ml water and 2 ml nitric acid were added, the solutions heated and treated with hydrogen sulfide as previously described. The precipitates of lead sulfide were filtered and washed as before. The acidity of the filtrate was maintained by the addition of 2 ml of nitric acid to the diluted solution, and the hydrogen sulfide treatment repeated. The second treatment produced only a small amount of lead sulfide as shown by a slight brown discoloration on the filter paper.

The lead sulfide and filter paper were digested for 30 minutes on the hot plate. Additional 1-1 acid was added from time to time. The solution was then diluted, filtered, and the precipitate washed. The filtrate was evaporated to dryness on the steam bath; the residue was ignited in platinum. The lead nitrate secured by evaporation was dissolved by the addition of water and transferred to the platinum crucibles in which the paper had been ignited. The solutions in the crucibles were evaporated to dryness. Dilute sulfuric acid was then added and fumed off in an air bath as described above. The crucibles were finally weighed and the per cent of lead calculated.

The filtrate containing thorium and uranium was diluted to 500 ml and 10 ml of concentrated hydrochloric

acid added. The solution was heated and 100 ml of hot 10 % oxalic acid added. One week was allowed for the precipitate to form. It was then filtered and washed. The precipitate and filter paper was returned to the precipitation beaker and treated with 25 ml of 1-1 nitric acid and one drop of 0.1 N potassium permanganate solution to catalyze the process of solution[1]. The thorium oxalate dissolved completely on the hot plate with the copious evolution of brown fumes.

The solution was evaporated to dryness on the steam bath. The residue was found to be insoluble in water, but soluble in dilute nitric acid. The solution was again evaporated to dryness. The residue was insoluble in water, only slightly soluble in acetic acid, and readily soluble in dilute nitric acid. The attempt to obtain a neutral, or acid free, solution was then abandoned.

The volume of the solution was made up to 50 ml and carefully neutralized with dilute ammonia to a methyl orange end point. Care must be taken in neutralizing with ammonia to avoid precipitation of the hydroxide. A slight excess of solid sebacic acid was added. The precipitate was digested a very few minutes on the hot plate, filtered, and washed

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[1] Hauser and Wirth: Zeitschrift fur Angewandte Chemie, 22: 12 Marz, (1909), 484 - 487

with hot water. The filtrate was treated with a large excess of ammonia and filtered to determine if any precipitate resulted.

The precipitates in each case were ignited. The residues from the ignition of the thorium sebacate weighed 0.00123 and 0.02531 grams respectively; and the residues from the ignition of the hydroxide precipitate weighed 0.00068 and 0.01129 grams respectively.

There is absolutely no agreement between the per cents of thorium found in this analysis. It was thought that the residue from sample 2 might have contained undecomposed sebacic acid in view of the larger residue obtained from the filtrate by precipitation with ammonia, although the time of ignition should have proved ample for its decomposition. Therefore 1 ml of concentrated nitric acid was added to each crucible and evaporated to dryness in an air bath. This process was repeated three times. The final weights of the crucibles, however, were practically unchanged. The variations in these results, therefore, are still unexplained.

The filtrate containing uranium was evaporated with nitric acid to destroy oxalic acid and finally was evaporated to dryness as previously described. The residue was taken up with water and transferred to a liter beaker. A solution of ammonium carbonate in 1-1 ammonia was added. There was no noticeable precipitate. The solution was filtered, and the small residue on the paper washed with

dilute ammonia solution containing ammonium carbonate.

The paper was dropped back into the beaker and nitric acid added to dissolve the precipitate. The solution was boiled, cooled, and treated again with ammonium carbonate and ammonia. The precipitate was washed and ignited in order to get an idea of the amount of this residue. The results indicate that this residue has a weight equal to about 8 % of the weight of the sample.

The treatment of the filtrate will be described later.

Second analysis

Samples 3 and 4 were weighed and dissolved in 50 ml of 1-1 nitric acid. The mixture was allowed to stand over night and then evaporated to dryness on the steam bath. A white residue of silica, colored green by uranium salts, was left. Water and dilute nitric acid were added and the solution again evaporated to dryness. Water and nitric acid were again added and the solution filtered. The residue was washed with hot water and ignited. The filtrate was again evaporated to dryness, the residue taken up in water and acid and filtered as before. The residue was ignited in the same crucibles used before. The ignited residue was pure white, but contained a few small black specks.

The residue was weighed, treated with sulfuric acid and hydrofluoric acid as previously described, and again ignited. The amount of silica was found to be so much higher than in the previous samples that it must be assumed that silica was dissolved from the beaker during the week long dehydration on the steam bath.

The lead was determined exactly as before.

The filtrate from which the lead had been removed was evaporated to dryness, diluted to 400 ml in a 600 ml beaker and 100 ml of 10 % oxalic acid added. The mixture was allowed to stand five days, then filtered and washed with a 2 % solution of oxalic acid containing a little hydrochloric acid. The filtrate containing uranium was treated with 100 ml of redistilled nitric acid and left on the hot plate (low heat). The precipitates of thorium oxalate were returned to the precipitation beakers. One drop of 0.1 N potassium permanganate solution and 45 ml of 1-3 nitric acid were added. The mixture was heated 30 minutes on the hot plate and then filtered into 250 ml beakers. The filtrate was evaporated to dryness on the steam bath; the residue was returned to the precipitation beaker, treated with 30 ml of concentrated nitric acid and one drop of potassium permanganate solution, and boiled for two hours. Brown fumes were evolved from the acid.

The mixture was then boiled for another hour, diluted to 100 ml and filtered into 600 ml beakers. The

residues were ignited in vitrosil crucibles. Since these residues were found to weigh 0.00033 and 0.00059 grams including the weight of the ash from four circles of filter paper, it is concluded that all of the oxalate precipitate was dissolved by the two treatments.

The first filtrates in 250 ml beakers were evaporated to dryness and dissolved in dilute nitric acid. It was intended to precipitate the thorium sebacate from faintly acid solution. Methyl red indicator, however, was bleached instantly by the solution. This was probably due to the presence of nitrous acid. The solution was therefore neutralized with dilute ammonia until a slight cloudiness appeared. This cloudiness was then cleared by the addition of 1-10 dilute nitric acid, drop by drop with stirring.

To the slightly acid solution thus obtained, an excess of solid sebacic acid was added. The precipitates were filtered, washed with boiling water, and ignited in platinum crucibles. The residues weighed 0.00677 and 0.00026 grams respectively.

The second filtrates, in the 600 ml beakers, were treated in the same way and the precipitates ignited. These precipitates were found to weigh 0.00003 and 0.00009 grams respectively. This indicates that all of the precipitate was dissolved by the first thirty minute's boiling.

The combined filtrates containing excess sebacic

acid were neutralized with excess ammonia, filtered, and ignited in vitrosil crucibles. It was noted that the solid sebacic acid dissolved in the ammonia. These combined filtrates should contain any thorium not precipitated as sebacate. This thorium should have been precipitated as $Th(OH)_4$ unless the hydroxide is soluble in ammonium sebacate. The ignited residues weighed 0.00064 and 0.00036 grams respectively.

The sum of the weights of the residues of thorium dioxide for samples 3 and 4 are therefore 0.0074 and 0.0006. This indicates that practically no thorium at all was recovered from sample 4.

The filtrates containing the uranium were evaporated with nitric acid and treated with ammonium carbonate as described above for samples 1 and 2. The purified filtrates from all four samples were evaporated to dryness with nitric acid several times to destroy ammonium salts. The uranium was precipitated with ammonia and the precipitates filtered and washed with hot 2 % ammonium nitrate solution. Uranium was recovered from the filtrate as described in the section on the preliminary analyses. The precipitates were ignited and weighed.

Third analysis

The ground sample was transferred to another weighing bottle of the type which has a cover fitting over the outside rim and dried one hour at 110° C in the oven. After cooling in the dessicator, samples 5 and 6 were weighed.

The beakers into which these samples were weighed had previously been cleaned, covered with watch glasses, dried on the hot plate, inverted on clean watch glasses, and allowed to stand under a bell jar until needed. The samples in the dry beakers were left covered under the bell jar until early morning. The entire process of dehydration was accomplished in one working day in order to minimize the solution of silica from the beakers.

The sides of the beakers were washed down by a stream from the wash bottle and 50 ml of 1-1 nitric acid were added (8:45 A.M.). A slight evolution of gas was noticed during solution in the cold. A white residue resembling silica was left. When solution was practically complete, the beakers were placed on the steam bath. After ten minutes no black specks were visible. The solution was green (uranium) and contained flashes of white residue (silica). The solution was evaporated on the steam bath and baked out for about an hour after it was completely dry. The residue was taken up in very dilute nitric acid and

filtered (4:30 P.M.). The residue was washed with warm very dilute (1 %) nitric acid and ignited.

The filtrate was evaporated to dryness and 10 ml of nitric acid were added. It was then evaporated to dryness again, baked one hour on the steam bath, diluted to 100 ml, heated, and filtered (Whatman # 42). The residue was washed with a volume of wash water which contained 1 ml of nitric acid. The filtrate was heated and 2 ml of nitric acid added. The solution was then treated with hydrogen sulfide.

The crucibles containing the silica weighed 24.41059 g and 24.14268 g after the first dehydration. After the second dehydration they weighed 24.41193 g and 24.14404 g, an increase in weight of 0.00134 g and 0.00136 g. This increase may have been due to separation of more silica, solution of silica from the beaker, or even occlusion of lead, thorium, or uranium.

The ash was treated with a few drops of sulfuric acid, fumed off, ignited, and weighed. This treatment caused practically no change in the weights: 24.41198 g and 24.14395 g. Hydrofluoric acid and sulfuric acid (1 ml each) were then added, fumed off, and ignited. When brought to constant weight, the weight of the silica was determined and the per cent of silica calculated. The mean was 1.872 % and the deviation from the mean was

two parts per thousand. These results are considered the most accurate expression of the silica content of the outside section.

The silica free filtrate was treated with hydrogen sulfide in the regular manner as described above and the lead determined as molybdate exactly as described in the preliminary work.

The uranium was determined exactly as before. Since the procedures were carried through more promptly and continuously and since all the operations proceeded more smoothly than in the case of samples 1-4, more confidence is felt in the results.

The thorium in samples 5 and 6 was not separated from rare earths. The oxalate precipitate was dissolved in dilute nitric acid with the aid of potassium permanganate. The filter paper pulp was filtered and the filtrate treated with ammonia. The precipitate was filtered, washed, and ignited. Calculations of impure thorium from the data indicated 1.656 % and 1.711 %. It is possible that the manganese interfered. These results show that the maximum amount of thorium is about 1.7 %

Fourth analysis

Two samples (7 and 8) from the outside section, four samples (9, 10, 11, and 12) from the middle section, and three samples (13, 14, and 15) from the core were weighed into 600 ml beakers.

Each beaker received 50 ml of 1-1 nitric acid and was placed on the steam bath for 24 hours. The solutions evaporated to dryness during this time. Then 10 ml of 10 % nitric acid were added and the solutions again evaporated to dryness. The residues were taken up in water, heated on the hot plate, filtered, and washed with hot water. The residues were ignited in platinum. The filtrates were evaporated again, the residues taken up in water, heated, filtered, and washed with hot water as above. None of the beakers showed any signs of etching. These residues were ignited in the proper crucibles, moistened with one drop of sulfuric acid, fumed off, and ignited to constant weight.

To each crucible were added 1 ml of hydrofluoric acid and 1 ml of sulfuric acid. The crucibles were placed in an air bath and the acids evaporated and fumed off. The loss of weight on ignition was assumed to be the weight of the silica and the per cents calculated.

The residues remaining from the hydrofluoric acid treatment were heated with dilute nitric acid and filtered

into the filtrate from which the silica had been removed. These solutions were then treated with hydrogen sulfide as before. The precipitates of lead sulfide were dissolved in nitric acid and the solution filtered. The paper was ignited in vitrosil crucibles and the residue treated with nitric acid. The solutions were washed into the corresponding lead nitrate solutions and the lead determined as molybdate.

The filtrates from which the lead had been removed were evaporated to dryness on the hot plate to expel hydrogen sulfide and nitric acid. The residue was taken up in hot water and heated on the hot plate. The solutions were diluted to 300 ml and 10 ml of hydrochloric acid and 100 ml of 10 % oxalic acid were added. The precipitates were allowed to digest for one week, part of the time on the hot plate; but the volume of the solution was kept at 400 ml by the addition of water when necessary.

The precipitates of thorium oxalate were filtered and treated with the phenylarsonic acid separation process as previously outlined. Each sample was treated essentially as described above, but there were some variations.

When the precipitates of thorium phenylarsonate were filtered through # 42 paper, the time required for filtering and washing exceeded six hours. Therefore samples 7, 8, 9, and 10 were filtered first through # 40

paper and then the filtrates refiltered through # 42 paper. Sample 11 was filtered through # 42 paper. The time available did not permit thorough washing; the final precipitate therefore was decidedly brown in color, indicating the presence either of rare earths or of arsenic. In the treatment of sample 12, the filter paper mass resulting from the hydrochloric acid solution was not removed by filtration. The final precipitate, therefore, was mixed with a large bulk of filter paper which retained a large amount of wash water. While inserting the filter into the crucible prior to ignition, the pressure of the finger caused some of this water to flow up and over the rim. The results of samples 11 and 12 were calculated, however, as a measure of the maximum and minimum to be expected. The residue from the ignition of sample 15 was a grayish brown color. Since it was obviously contaminated, the results should be discarded.

The filtrate from which thorium oxalate had been filtered was evaporated to a very small volume several times with nitric acid to destroy the excess oxalic acid. The residue was taken up in water and treated with ammonia and ammonium carbonate as before. The purified filtrate was evaporated to dryness several times with nitric acid to destroy ammonium salts. The uranium was then separated with ammonia as above and ignited to U_3O_8.

SUMMARY OF RESULTS

Sample number	Weight of sample	Weight of silica	Per cent of silica	Weight of lead ppt.	Per cent of lead
		Outside Section			
				$PbSO_4$	
1	0.56329	0.01269	2.253	0.03110	3.772
2	1.47361	0.03272	2.220	0.07487	3.472
3	0.8662	0.05515	6.40	0.04159	3.280
4	0.9893	0.07334	7.41	0.04917	3.396
				$PbMoO_4$	
5	1.19235	0.02227	1.868	0.06779	3.210
6	0.95887	0.01799	1.876	0.05345	3.146
7	1.09214	0.02324	2.128	0.06175	3.191
8	0.67942	0.01596	2.349	0.03858	3.205
		Middle Section			
9	0.66562	0.01224	1.839	0.03988	3.381
10	0.94661	0.01661	1.755	0.05684	3.389
11	1.10762	0.01772	1.600	0.06663	3.395
12	1.26772	0.02322	1.832	0.07557	3.364
		Core			
13	0.97833	0.01486	1.519	0.06001	3.462
14	0.91160	0.01444	1.584	0.05566	3.446
15	1.59226	0.02261	1.420	0.09677	3.430

Sample number	Weight of ThO_2	Per cent of thorium	Weight of U_3O_8	Per cent of uranium
		Outside Section		
1			0.45040	67.81
2			1.17020	67.34
3			0.69722	68.26
4			0.78922	67.65
5			0.95197	67.74
6			0.76509	67.66
7	0.00039	0.03	0.86977	67.54
8	0.00019	0.02	0.54865	68.48
		Middle Section		
9	0.00083	0.11	0.54857	69.89
10	0.00138	0.13	0.78128	69.99
11	0.01106	0.88	0.91296	69.90
12	0.00091	0.06	1.01364	67.81 (spattering)
		Core		
13	0.00021	0.02	0.80252	69.57
14	0.00032	0.03	0.74893	69.67
15	0.00144	0.08	1.30885	69.71

The following results are considered accurate

Section of crystal	Sample number	Per cent of silica	Per cent of lead	Per cent of thorium	Per cent of uranium
Outside	5	1.87	3.21		67.74
	6	1.88	3.15		67.66
	7	2.13	3.19	0.03	67.54
	8	2.35	3.21	0.02	
Middle	9	1.83	3.38	0.11	69.89
	10	1.76	3.39	0.13	69.99
	11	1.60	3.40		69.90
	12	1.83	3.36		
Core	13	1.52	3.46	0.02	69.57
	14	1.59	3.45	0.03	69.67
	15	1.42	3.43		69.71

Averages

Outside	2.06	3.19	0.03	67.65
Middle	1.76	3.38	0.12	69.93
Core	1.51	3.45	0.03	69.65

If these values are substituted in the formula referred to in the Introduction, the following values for the lead ratio and for the age of the sections are obtained:

	Lead ratio	Age
Outside section	0.04715	358 million years
Middle section	0.04831	367 million years
Core	0.04953	376 million years

DISCUSSION OF RESULTS AND CONCLUSIONS

Since solutions prepared in glass vessels are always likely to dissolve some silica, the amounts of silica reported above cannot be considered extremely accurate. This is very evident from the results of uraninite samples 3 and 4, in which the separation of silica was delayed. All other analyses for silica were carried out as rapidly as possible and are probably close to the true value. They are undoubtedly slightly high, however.

The separation of lead as sulfide seems entirely satisfactory. The final determination of lead as molybdate is more convenient than as sulfate. The results of the analysis of the second prepared solution (samples 21, 22, 25, and 26) indicate that lower results may be expected from the molybdate method. The percentages of lead found in the uraninite, therefore, may be slightly low: perhaps by nine parts in a thousand.

The separation of thorium as oxalate is much slower than has been indicated in the literature. The data from the analysis of the second prepared solution show that results, even when several days have been allowed for the precipitate to form may be low by as much as 28 parts in a thousand.

So much difficulty was experienced in the application of the sebacic acid method that this procedure is not recommended for the determination of thorium. The phenylarsonic acid method, although slow and tedious, gave results which checked exactly within the limits of accurate weighing. If the cost of the precipitant is disregarded, the method is very satisfactory.

The separation of uranium as ammonium uranate and subsequent ignition to uranium oxide, U_3O_8, is simple and accurate. It is believed that the results are quite dependable.

The amount of thorium is so small that an error in its determination is insignificant as far as age calculations from this mineral are concerned. Even in minerals where the amount is larger, any error would be diminished since the quantity is multiplied by the factor 0.36. An absolute variation of 0.1 % in the value for lead in this mineral would cause a difference in the age of only about ten million years. It is believed, however, that the absolute error does not exceed 0.05 %.

It may be concluded that the methods for the determination of the lead - uranium - thorium ratio of uranium minerals outlined above and applied to the analysis of uraninite from Spruce Pine, North Carolina, are satisfactory and reliable.

THREE

GENERAL PART

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THE EFFECT OF AMMONIUM CHLORIDE WASH SOLUTION ON THE QUANTITATIVE GRAVIMETRIC DETERMINATION OF IRON AND THE LEAD-URANIUM-THORIUM RATIO OF URANINITE FROM SPRUCE PINE, NORTH CAROLINA

Abstract of a Dissertation

Submitted in partial fulfilment of the requirements for the degree of
Doctor of Philosophy

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A. *The Effect of Ammonium Chloride Wash Solution on the Quantitative Gravimetric Determination of Iron*

There is wide variation in the practise of washing the precipitate of hydrated ferric oxide in the gravimetric determination of iron. Some authors recommend the use of ammonium chloride; some, ammonium nitrate; some, ammonium hydroxide; and some, hot water.

A rather extensive study was made of the effects of these washing solutions, particularly ammonium chloride, in concentrations of from 1 to 5 per cent. Ten gram samples of a ferric nitrate solution were weighed by difference from a weight buret, diluted to 190 ml, treated while cold with 10 ml of freshly distilled ammonia, and digested on the steam bath for one hour. A firm precipitate which could be readily retained by #40 Whatman filter paper was obtained.

The precipitate on the filter was washed repeatedly with the selected washing solution, allowed to drain thoroughly, and ignited. The results show that ammonium chloride solutions are not suitable even in concentrations as low as 1%, especially if the filter paper is slowly charred. The error is less if very rapid charring is effected. If higher concentrations of ammonium chloride are employed, the error is likely to be appreciable even with rapid charring. The error is due to volatilization of ferric chloride.

Good results were obtained by the use of 1.37% ammonia solution, but this solution is not to be recommended due to its possible solvent action on the glass container during the digestion of the precipitate. In spite of the extreme insolubility of the ferric oxide, the results obtained when the precipitates were washed with hot water were low. This loss was probably due to the peptization of the colloidal precipitate which permitted it to pass through the filter paper. One per cent. ammonium nitrate solution was found to give the most precise and reliable results. This solution is not only an efficient washing solution, but the presence of ammonium nitrate apparently has a beneficial effect on the subsequent ignition of the filter paper and precipitate. Such a solution is recommended over all others in common use in the gravimetric determination of iron.

B. *The Lead-Uranium-Thorium Ratio of Uraninite from Spruce Pine, North Carolina*

Numerous attempts have been made to estimate the age of the earth from such processes as the rate of cooling of the earth, the rate of sedimentation, or the rate of accumulation of salt in the ocean. Perhaps the most accurate method is one suggested by Boltwood which depends on the determination of the lead produced by the radioactive disintegration of thorium and uranium in minerals. It can be shown that the approximate age of a given mineral can be calculated from the formula

$$\text{Age} = \frac{\text{Pb}}{\text{U} + 0.36\ \text{Th}} \times 7600 \text{ million years}$$

Obviously the formula is worthless unless the amounts of lead, uranium, and thorium can be accurately determined. The task of examining some of the analytical methods for the determination of these elements was therefore undertaken. The methods which seemed most satisfactory were finally applied to the analysis of a sample of uraninite from Spruce Pine, North Carolina.

Suitable quantities of lead nitrate, uranium nitrate, and thorium nitrate were carefully purified and a standard solution containing known amounts of these salts was prepared.

Lead was separated from this solution by the action of hydrogen sulfide and its determination as sulfate, molybdate, and chromate was investigated. The lead sulfide was dissolved in nitric acid and the resulting lead nitrate solution evaporated to dryness, in successive portions, in a crucible. Dilute sulfuric acid was then added and the crucible heated in an air bath until the lead sulfate produced was completely dry and at constant weight. The best results for lead by this method were four parts per thousand low.

A solution of lead nitrate prepared in the same manner was buffered with ammonium acetate and the lead precipitated with 2.5% ammonium molybdate solution. Ammonia was added and the precipitate, after digestion for one hour on the hot plate, was filtered, washed with 2% ammonium nitrate, and ignited. The procedure is simple and rapid. The results were eight parts per thousand low.

Lead chromate was precipitated from the lead nitrate solution with 5% ammonium chromate. The precipitate tended to creep and to run through the filter. The results obtained were twenty-two parts per thousand low.

Thorium was separated as oxalate. The precipitate requires at least five days to form, and even then the results may be low by as much as twenty-eight parts per thousand. Thorium oxalate is not readily soluble in 1-1 nitric acid. It will dissolve in the concentrated acid, but a precipitate will separate if the solution is diluted. A solution can be obtained in 1-1 HNO_3 if one drop of .1 N $KMnO_4$ is added. This solution can be diluted.

The determination of thorium and its separation from rare earths by precipitation as sebacate according to the method of Smith and James was investigated at length, but no satisfactory results could be obtained. The method is not recommended.

Good results were obtained by precipitation by phenylarsonic acid in the presence of sulfurous acid, glacial acetic acid, and ammonium acetate. The resulting mixture is so viscous that filtration through Whatman #42 paper is extremely slow, yet Whatman #40 paper will not remove all of the fine precipitate. It is therefore advisable to filter the solution first through #40 paper and then to refilter it through #42 paper. After two precipitations as phenylarsonate, the precipitate was dissolved in hydrochloric acid and reprecipitated as oxalate. The oxalate was then ignited to ThO_2. Results obtained by the application of the method to pure thorium nitrate solutions checked almost exactly with the results obtained by precipitation as oxalate and direct ignition to ThO_2.

The filtrate from the thorium precipitation was evaporated with concentrated nitric acid to destroy the oxalic acid. Uranium was then separated from iron and other impurities by treatment with a solution of ammonium carbonate and ammonia. Uranium does not precipitate under these conditions.

The mixture was filtered and the filtrate evaporated with nitric acid to expel CO_2. The uranium was then precipitated by the addition of freshly distilled ammonia. The precipitate was ignited to U_3O_8. The results for uranium were three parts per thousand high.

A sample of uraninite from Spruce Pine, North Carolina, was then analyzed by the methods outlined above. The crystal had been divided into three layers with a file, so that the possibility of leaching could be considered.

The sample was dissolved in nitric acid and evaporated to dehydrate the silica. The insoluble material was filtered off and the silica determined by loss of weight on treatment with HF. The residue was extracted with HNO_3 and the solution obtained was added to the main filtrate. Lead was then removed as sulfide and determined as sulfate or molybdate; thorium was removed as oxalate, separated from rare earths by the phenylarsonic acid process, again precipitated as oxalate, and ignited to the oxide; uranium was purified by treatment with ammonium carbonate and ammonia, precipitated as ammonium uranate, and ignited to U_3O_8.

The following results were obtained:

Section of crystal	Per cent. of silica	Per cent. of lead	Per cent. of thorium	Per cent. of uranium
Outside	2.06	3.19	0.03	67.65
Middle	1.76	3.38	0.12	69.93
Core	1.51	3.45	0.03	69.65

If these values are substituted in the formula referred to above, the following values for the lead ratio, Pb/ (U + 0.36 Th), and for the age of the sections are obtained:

	Lead ratio	Age
Outside section	0.04715	358 million years
Middle section	0.04831	367 million years
Core	0.04953	376 million years

Additional copies may be obtained on application to
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